09

Redox processes

Essential ideas

9.1 Redox (reduction–oxidation) reactions play a key role in many chemical and biochemical processes.

9.2 and 19.1 Voltaic cells convert chemical energy to electrical energy and electrolytic cells convert electrical energy to chemical energy. Energy conversions between electrical and chemical energy lie at the core of electrochemical cells.

Oxygen makes up only about 20% by volume of the air, yet it is the essential component for so many reactions. Without it fuels would not burn, iron would not rust, and we would be unable to obtain energy from our food molecules through respiration. Indeed, animal life on the planet did not evolve until a certain concentration of oxygen had built up in the atmosphere over 600 million years ago. The term **oxidation** has been in use for a long time to describe these and other reactions where oxygen is involved in chemical change. Oxidation, though, is only half of the story, as it is always accompanied by the opposite process **reduction**, which was originally thought of in terms of loss of oxygen.

Later, however, the terms widened to include a much broader range of reactions. We now define these two processes, oxidation and reduction, as occurring whenever electrons are transferred from one reactant to another – and many of these reactions do not use oxygen. For example, photosynthesis, the process by which plants store chemical energy from light energy, involves oxidation and reduction reactions, although oxygen itself is not a reactant.

Transferring electrons from one substance to another leads to a flow of electrons, in other words an electric current. So, chemical reactions can be used to generate electricity – a simple **voltaic cell** or **battery** works in this way. By reversing the process and using an electric current to drive reactions of oxidation and reduction, stable compounds can be broken down into their elements. This is the process known as **electrolysis**. These applications of oxidation and reduction, collectively known as **electrochemical cells**, have truly revolutionized our world. For example, it would be hard to imagine life without the many battery-powered mobile devices we use every day, or without metals such as aluminium that are only available from electrolysis. An understanding of oxidation and reduction is therefore at the heart of the study of a large branch of chemistry both in the laboratory and beyond.

The vigorous reaction here shows the redox change that occurs when magnesium metal and copper oxide are heated together, forming magnesium oxide and copper. $Mg(s) + CuO(s) \rightarrow MgO(s) + Cu(s)$.
Redox reactions occur when electrons are transferred between species, and are the basis of electrochemistry.

Coloured X-ray of a smart phone, showing its rechargeable battery. Mobile devices such as this are powered by electrical energy generated from the reactions of oxidation and reduction occurring within the battery.

▼
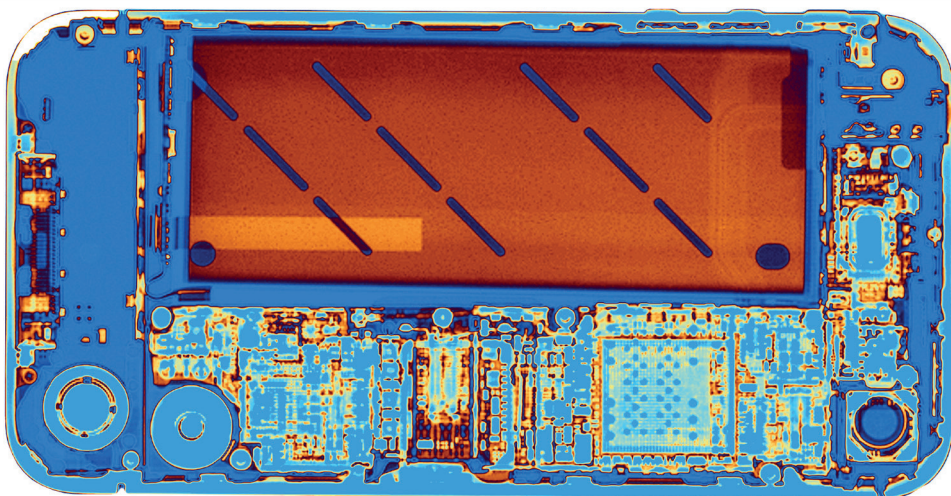
9.1 Oxidation and reduction

Understandings:
- Oxidation and reduction can be considered in terms of oxygen gain/hydrogen loss, electron transfer, or change in oxidation number.
- An oxidizing agent is reduced and a reducing agent is oxidized.

  Guidance
  Oxidation states should be represented with the sign given before the number, e.g. +2 not 2+.

- Variable oxidation numbers exist for transition metals and for most main-group non-metals.

  Guidance
  The oxidation state of hydrogen in metal hydrides (−1) and oxygen in peroxides (−1) should be covered.

- The activity series ranks metals according to the ease with which they undergo oxidation.

  Guidance
  A simple activity series is given in the IB data booklet in section 25.

- The Winkler method can be used to measure biochemical oxygen demand (BOD), used as a measure of the degree of pollution in a water sample.

Applications and skills:
- Deduction of the oxidation state of an atom in an ion or a compound.
- Deduction of the name of a transition metal compound from a given formula, applying oxidation numbers represented by Roman numerals.

  Guidance
  Oxidation number and oxidation state are often used interchangeably, though IUPAC does formally distinguish between the two terms. Oxidation numbers are represented by Roman numerals according to IUPAC.

- Identification of the species oxidized and reduced and the oxidizing and reducing agents, in redox reactions.
- Deduction of redox reactions using half-equations in acidic or neutral solutions.
- Deduction of the feasibility of a redox reaction from the activity series or reaction data.
- Solution of a range of redox titration problems.
- Application of the Winkler method to calculate BOD.

Introduction to oxidation and reduction

Early attempts to define oxidation and reduction were based on observations of the gain and loss of oxygen and hydrogen during chemical change. They can be summarized as follows.

Oxidation	Reduction
gain of oxygen	loss of oxygen
loss of hydrogen	gain of hydrogen

These definitions are still useful in some cases, particularly in organic chemistry, but they have largely been replaced by a more inclusive approach. It is now recognized that oxidation and reduction occur during chemical change whenever there is a shift in electron density from one atom to another. In other words, the focus has become the transfer of electrons, whether complete or partial, whether oxygen and hydrogen are involved or not. Some examples will help to explain this.
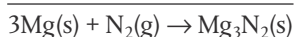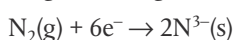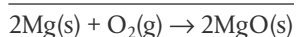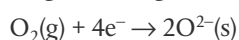
When magnesium is burned in air, it gives a bright white flame with the production of a white powder, magnesium oxide:

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$
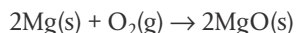
The fact that magnesium gains oxygen in this reaction makes it easy to see why we say it is an **oxidation** reaction and that magnesium has been oxidized. However, during the same reaction a small amount of the magnesium combines with the nitrogen of the air too, forming magnesium nitride. It may be less obvious that this is also an oxidation reaction and that again magnesium is oxidized.

$$3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$$
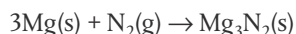
What do these two reactions have in common which means they can both be defined in this way? If we divide them into so-called **half-equations**, each showing what happens to one reactant, we can examine what is happening in terms of electrons.

$$2Mg(s) \rightarrow 2Mg^{2+}(s) + 4e^-$$
$$\underline{O_2(g) + 4e^- \rightarrow 2O^{2-}(s)}$$
$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

$$3Mg(s) \rightarrow 3Mg^{2+}(s) + 6e^-$$
$$\underline{N_2(g) + 6e^- \rightarrow 2N^{3-}(s)}$$
$$3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$$

In both reactions Mg is forming Mg^{2+} by losing electrons, while O and N are forming O^{2-} and N^{3-} respectively by gaining electrons. It is this transfer of electrons that now defines oxidation, and its opposite reaction, reduction.

❝ Oxidation is the loss of electrons, reduction is the gain of electrons. ❞

So in the reactions above, magnesium is oxidized while oxygen and nitrogen are reduced. Clearly each process is dependent on the other, so oxidation and reduction will always occur together and reactions of this type are known as **redox reactions**.

▲ Magnesium ribbon burning in air. It forms mostly magnesium oxide with small amounts of magnesium nitride.

It may help you to remember OILRIG: Oxidation Is Loss (of electrons), Reduction Is Gain (of electrons).

The free-radical theory of ageing suggests that the physiological changes associated with ageing are the result of oxidative reactions in cells causing damage to membranes and large molecules such as DNA. These changes accumulate with time and may explain the increase in degenerative diseases, such as cancer, with age. The theory suggests that supplying cells with anti-oxidants will help to slow down the damaging oxidative reactions. Anti-oxidants are particularly abundant in fresh fruit and vegetables, as well as in red wine, tea, and cocoa. Although there is strong evidence that anti-oxidant supplementation may help protect against certain diseases, it has not yet been shown to produce a demonstrated increase in the human life span.


▲ Fresh fruits and vegetables are good sources of anti-oxidants, which may help prevent damaging oxidative reactions in cells.

Oxidation is the loss of electrons, reduction is the gain of electrons.

Oxidation numbers enable us to track redox change

In reactions involving ions, such as the examples above, it is easy to identify the electron transfers occurring. But what about reactions where electrons are not transferred but instead are shared in a covalent bond, such as the combination of hydrogen and oxygen to produce water? Can oxidation and reduction be identified here too?

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$
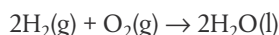
The answer is 'yes', through the introduction of the concept of **oxidation state**. This is a value we assign to each atom in a compound that is a measure of the electron control or possession it has relative to the atom in the pure element. Oxidation state can be defined as the apparent charge that an atom has in a molecule or ion. It is as if we exaggerate the unequal sharing in a covalent bond, based on electronegativity differences, to the point where each atom has complete gain or loss of the electrons shared – in other words, has formed ions. This enables us to keep track of the relative electron density in a compound and how it changes during a reaction. There are two parts to the oxidation state:
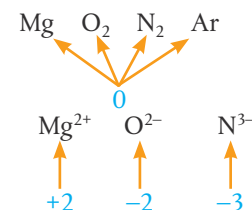
- the sign: '+' means the atom has lost electron control, '–' means it has gained electron control;
- its value: this refers to the number of electrons over which control has changed.

The oxidation state is written with the sign first, followed by the number, e.g. +2 or −3.

Strategy for assigning oxidation states

There are a few simple rules to follow which help in determining the oxidation state of an atom in any species. We will use blue to show oxidation states throughout this text.

1 Atoms in the free (uncombined) element have an oxidation state of zero: for example,

$Mg \quad O_2 \quad N_2 \quad Ar$
0

2 In simple ions, the oxidation state is the same as the charge on the ion: for example,

$Mg^{2+} \quad O^{2-} \quad N^{3-}$
$+2 \quad\quad -2 \quad\quad -3$

3 The oxidation states of all the atoms in a neutral (uncharged) compound must add up to zero:
   for example, in H_2SO_4 the sum of oxidation states = 0.

4 The oxidation states of all the atoms in a polyatomic ion must add up to the charge on the ion:
   for example, in SO_4^{2-} the sum of oxidation states = −2.

5 The usual oxidation state for an element is the same as the charge on its most common ion:
   for example, Group 1 elements have oxidation state = +1, H is usually +1, O is usually −2.

6 Most main group non-metals, the elements at the bottom of Group 14, and transition elements have oxidation states that vary in different compounds – depending on the conditions and other elements present. So for N, P, S, Sn, Pb, and all transition elements, the oxidation state of the element in a particular species needs to be determined on a case-by-case basis.

The table on page 409 summarizes some useful information about oxidation states.

Note that the charge on an ion X is written with the number first then the charge: e.g. X^{2+}. The oxidation state is written with the charge first then the number: e.g. +2.

What ways of knowing can we use to distinguish between the charge on an ion and the oxidation state?

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Element	Usual oxidation state	Exceptions	Explanation
Li, Na, K	+1		
Mg, Ca	+2		
F	−1		there are no exceptions because F is the most electronegative element
O	−2	peroxides such as H_2O_2, where it is −1; OF_2, where it is +2	
H	+1	metal hydrides such as NaH, where it is −1	H is more electronegative than Na and so gains electron control
Cl	−1	when it is combined with O or F	Cl is less electronegative than O and F, and so loses electron control

When working out the oxidation states of atoms in compounds, it is usually best to assign the oxidation state to the atoms that are easy to predict first, then use Rules 3 and 4 above to find the more unpredictable elements by subtraction.

Worked example

Assign oxidation states to all the elements in (a) H_2SO_4 and (b) SO_3^{2-}.

Solution

(a) We can assign H and O as follows: H_2SO_4

+1 −2

Note that the oxidation states apply to each atom and that here the sum of all the oxidation states must be zero as H_2SO_4 is electrically neutral.

Therefore, $2(+1) + S + 4(-2) = 0 \Rightarrow S = +6$

(b) Here we start by assigning O: SO_3^{2-}

−2

Note that here the oxidation states must add up to −2, the charge on the ion.

Therefore, $S + 3(-2) = -2 \Rightarrow S = +4$

The oxidation state of a transition metal in a complex ion can be worked out from the charges on the ligands and the overall charge. Remember from Chapter 3 that ligands are either neutral or negatively charged.

Worked example

Assign oxidation states to the metal ion in (a) $[Co(NH_3)_6]^{3+}$ and (b) $[CuCl_4]^{2-}$.

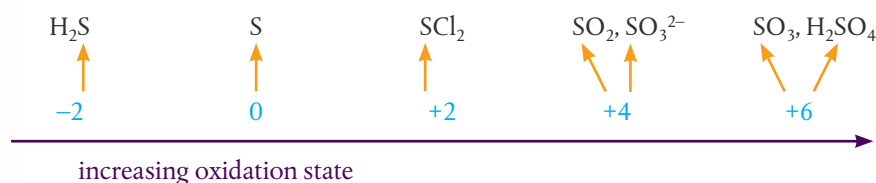### Solution

(a) NH_3 is a neutral ligand, so the charge on the complex is the same as the charge on the metal ion: ∴ Co = +3

(b) Cl has a 1− charge ∴ (charge on Cu) + (4 × 1−) = 2−

∴ Cu = +2

Interpreting oxidation states

We can see that an element such as sulfur can have a wide range of oxidation states in different compounds.

H_2S	S	SCl_2	SO_2, SO_3^{2-}	SO_3, H_2SO_4
-2	0	$+2$	$+4$	$+6$

increasing oxidation state

What is the significance of these different values? Because the oxidation state is a measure of the electron control that an atom has, it follows that the higher the positive number, the more the atom has lost control over electrons, in other words the more oxidized it is. Likewise, the greater the negative number, the more it has gained electron control, so the more reduced it is. Therefore H_2S represents sulfur in its most reduced form (lowest oxidation number), and SO_3 and H_2SO_4 represent sulfur in its most oxidized form (highest oxidation number).

It follows that any change in oxidation states during a reaction is an indication that redox processes are occurring: an increase in oxidation number represents oxidation, and a decrease in oxidation number represents reduction.

So, going back to the reaction between hydrogen and oxygen discussed earlier, we can now clearly follow the redox process:
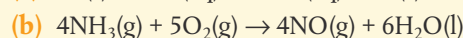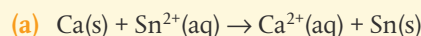
$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$
$$0 \qquad 0 \qquad +1 \;\; -2$$
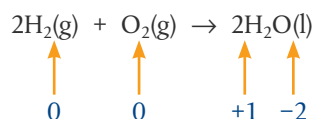
Hydrogen has been oxidized (oxidation state increased from 0 to +1) and oxygen has been reduced (oxidation state decreased from 0 to −2).

> **A redox reaction is a chemical reaction in which changes in the oxidation states occur.**
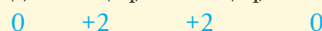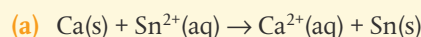
> **Oxidation occurs when there is an increase in oxidation state of an element, reduction occurs when there is a decrease in oxidation state of an element.**

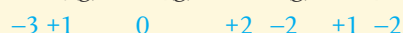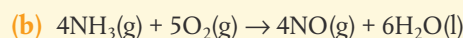### Worked example

Use oxidation states to deduce which species is oxidized and which is reduced in the following reactions:

(a) $Ca(s) + Sn^{2+}(aq) \rightarrow Ca^{2+}(aq) + Sn(s)$

(b) $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$

Solution

(a) $Ca(s) + Sn^{2+}(aq) \rightarrow Ca^{2+}(aq) + Sn(s)$
$\qquad 0 \qquad +2 \qquad +2 \qquad 0$
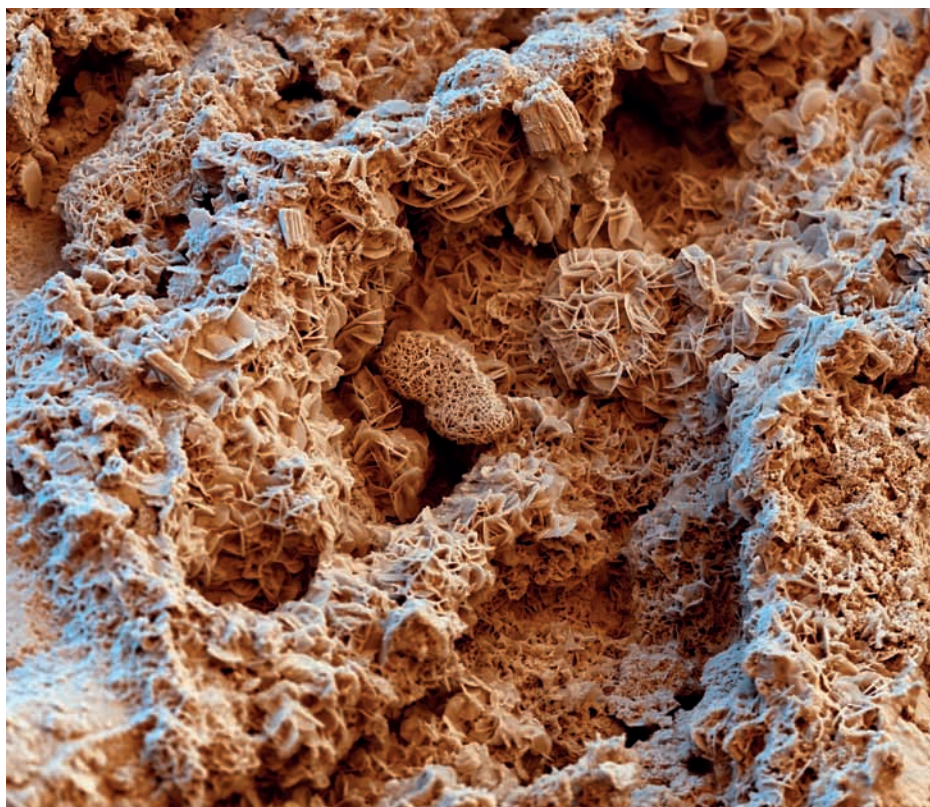
Ca is oxidized because its oxidation state increases from 0 to + 2; Sn^{2+} is reduced because its oxidation state decreases from +2 to 0.

(b) $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$
$\qquad -3 \;\; +1 \qquad 0 \qquad +2 \;\; -2 \quad +1 \;\; -2$

NH_3 is oxidized because the oxidation state of N increases from −3 to +2; O_2 is reduced because its oxidation state decreases from 0 to −2.

Coloured scanning electron micrograph (SEM) of rust on painted sheet metal. Rust is hydrated iron oxide resulting from electrochemical reactions between iron and atmospheric water vapour and oxygen. Rusting spontaneously causes iron to revert to its more stable oxidized state, unless this is prevented by protecting the iron. Rust flakes off the surface of the iron, causing it to be degraded and weakened.

Systematic names of compounds use oxidation numbers

We have seen that elements such as sulfur exhibit different oxidation states in different compounds. In these cases it is useful to include information about the oxidation state in the name. Traditional names used descriptive language that became associated with a particular oxidation state. For example, ferrous and ferric iron oxides referred to FeO and Fe_2O_3, in which Fe has oxidation states $+2$ and $+3$ respectively.

The IUPAC system, founded in 1919, introduced a nomenclature using **oxidation numbers** to make the names more recognizable and unambiguous. This system uses a Roman numeral corresponding to the oxidation state which is inserted in brackets after the name of the element. For example copper(I) oxide contains copper in the oxidation state $+1$. Different compounds in which the same elements have different oxidation states are then shown with different oxidation numbers, such as copper(I) oxide and copper(II) oxide.

Oxidation state is shown with a '+' or '–' sign and an Arabic numeral, e.g $+2$.

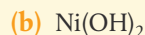Oxidation number is shown by inserting a Roman numeral in brackets after the name or symbol of the element.

The table shows some common examples.

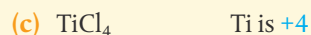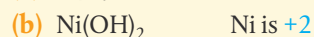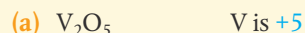| Formula of compound	Oxidation state	Name using oxidation number	Formula of compound	Oxidation state	Name using oxidation number
FeO	Fe +2	iron(II) oxide	MnO_4^-	Mn +7	manganate(VII) ion
Fe_2O_3	Fe +3	iron(III) oxide	$K_2Cr_2O_7$	Cr +6	potassium dichromate(VI)
Cu_2O	Cu +1	copper(I) oxide	Cr_2O_3	Cr +3	chromium(III) oxide
CuO	Cu +2	copper(II) oxide	NO	N +2	nitrogen(II) oxide
MnO_2	Mn +4	manganese(IV) oxide	NO_2	N +4	nitrogen(IV) oxide

Worked example

Deduce the name of the following compounds using oxidation numbers.

(a) V_2O_5 **(b)** $Ni(OH)_2$ **(c)** $TiCl_4$

Solution

1 First deduce the oxidation state:
   (a) V_2O_5 V is +5
   (b) $Ni(OH)_2$ Ni is +2
   (c) $TiCl_4$ Ti is +4

2 Then the corresponding Roman numeral is inserted after the name of the element. There is no space between the name and the number, and the number is placed in brackets.
   (a) vanadium(V) oxide
   (b) nickel(II) hydroxide
   (c) titanium(IV) chloride
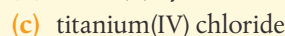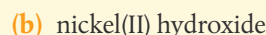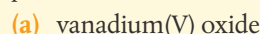
Although this nomenclature can theoretically be used in the naming of all compounds, it is really only worthwhile when an element has more than one common oxidation state. For example Na_2O could be called sodium(I) oxide, but as we know Na always has oxidation state +1, it is perfectly adequate to call it simply sodium oxide.

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Oxidation state and formal charge (introduced in Chapter 4) are both useful tools for electron book-keeping, but they are based on very different premises. Oxidation state is derived by assuming bonds are ionic unless they are between the same element; formal charge is assigned by assuming bonds are pure covalent. Each model has its usefulness and its limitations, as discussed on pages 193 and 415.

Redox equations

Writing half-equations

Although we have seen that oxidation cannot take place without reduction and vice versa, it is sometimes useful to separate out the two processes from a redox equation and write separate equations for the oxidation and reduction processes. These are therefore called **half-equations**. Electrons are added on one side of each equation to balance the charges.

Worked example

Deduce the two half-equations for the following reaction

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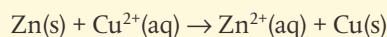
Solution

Assign oxidation states so we can see what is being oxidized and what is reduced.

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$
$$0 \qquad +2 \qquad\quad +2 \qquad\quad 0$$
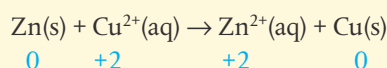
Here we can see that Zn is being oxidized and Cu^{2+} is being reduced.

oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ electrons are lost

reduction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ electrons are gained

Note there must be equal numbers of electrons in the two half-equations, so that when they are added together the electrons cancel out.

Writing redox equations using half-equations

Sometimes we may know the species involved in a redox reaction, but not the overall equation so we need to work this out, making sure it is balanced for both atoms and charge. A good way to do this is to write half-equations for the oxidation and reduction processes separately, and then add these two together to give the overall reaction. Many of these reactions take place in acidified solutions and we therefore use H_2O and/ or H^+ ions to balance the half-equations. The process is best broken down into a series of steps, as shown in the example below.
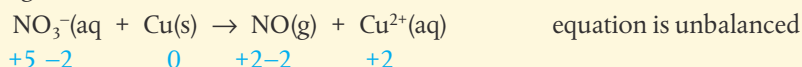
Worked example

Write an equation for the reaction in which NO_3^- and Cu react together in acidic solution to produce NO and Cu^{2+}.
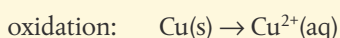
Solution

1   Assign oxidation states to determine which atoms are being oxidized and which are being reduced:

$$NO_3^-(aq + Cu(s) \rightarrow NO(g) + Cu^{2+}(aq)$$ equation is unbalanced
$$+5 \ -2 \qquad 0 \qquad +2 -2 \qquad +2$$

Therefore Cu is being oxidized ($0 \rightarrow +2$) and N is being reduced ($+5 \rightarrow +2$).
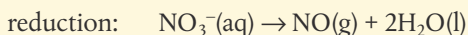
2   Write half-equations for oxidation and reduction.
  (a) Balance the atoms other than H and O:
        oxidation: $Cu(s) \rightarrow Cu^{2+}(aq)$
        reduction: $NO_3^-(aq) \rightarrow NO(g)$
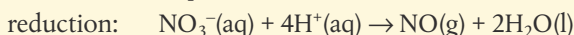   In this example the Cu and N are already balanced.
  (b) Balance each half-equation for O by adding H_2O as needed.
      Here the reduction equation needs two more O atoms on the right-hand side:
        reduction: $NO_3^-(aq) \rightarrow NO(g) + 2H_2O(l)$
  (c) Balance each half-equation for H by adding H^+ as needed.
      Here the reduction equation needs four H atoms on the left-hand side:
        reduction: $NO_3^-(aq) + 4H^+(aq) \rightarrow NO(g) + 2H_2O(l)$
  (d) Balance each half-equation for charge by adding electrons to the side with the more positive charge. (Electrons will be products in the oxidation equation and reactants in the reduction equation.)
        oxidation: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
        reduction: $NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$
  (e) Now check that each half-equation is balanced for atoms and for charge.
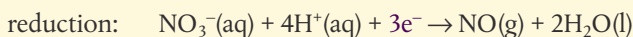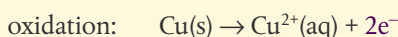
Photochromic lenses darken in response to increasing light intensity and become lighter in dim light. The change is brought about by a redox reaction between silver chloride and copper(I) chloride, which are both embedded in the lens. In bright light Ag^+ ions oxidize Cu^+ forming Ag and Cu^{2+}:

$$Ag^+(s) + Cu^+(s) \rightarrow Ag(s) + Cu^{2+}(s)$$
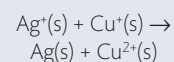
The silver metal produced creates a film over the lens, cutting out glare. In dim light the reaction reverses as Cu^{2+} oxidizes Ag, and the lens clears.

3 Equalize the number of electrons in the two half-equations by multiplying each appropriately.

Here the equation of oxidation must be multiplied by 3, and the equation of reduction by 2, to give six electrons in both equations:
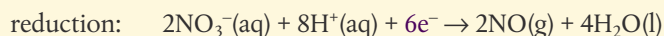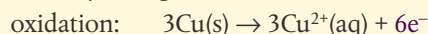
oxidation: $3Cu(s) \rightarrow 3Cu^{2+}(aq) + 6e^-$

reduction: $2NO_3^-(aq) + 8H^+(aq) + 6e^- \rightarrow 2NO(g) + 4H_2O(l)$

4 Add the two half-equations together, cancelling out anything that is the same on both sides, which includes the electrons.

$$3Cu(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Cu^{2+}(aq) + 2NO(g) + 4H_2O(l)$$
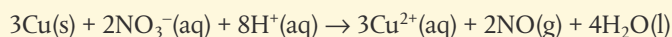
The final equation should be balanced for atoms and charge and have no electrons.

Summary of steps in writing redox equations.

1 Assign oxidation states to determine which atoms are being oxidized and which are being reduced.

2 Write half-equations for oxidation and reduction as follows:

(a) balance the atoms other than H and O;

(b) balance each half-equation for O by adding H_2O as needed;

(c) balance each half-equation for H by adding H^+ as needed;

(d) balance each half-equation for charge by adding electrons to the sides with the more positive charge.

(e) check that each half-equation is balanced for atoms and for charge.

**3** Equalize the number of electrons in the two half-equations by multiplying each appropriately.

4 Add the two half-equations together, cancelling out anything that is the same on both sides.

Exercises

1 Assign oxidation states to all elements in the following compounds:

(a) NH_4^+ (d) SO_2 (g) MnO_2 (i) $K_2Cr_2O_7$

(b) $CuCl_2$ (e) Fe_2O_3 (h) PO_4^{3-} (j) MnO_4^-

(c) H_2O (f) NO_3^-

2 Use oxidation states to deduce which species is oxidized and which is reduced in the following reactions:

(a) $Sn^{2+}(aq) + 2Fe^{3+}(aq) \rightarrow Sn^{4+}(aq) + 2Fe^{2+}(aq)$

(b) $Cl_2(aq) + 2NaBr(aq) \rightarrow Br_2(aq) + 2NaCl(aq)$

(c) $2FeCl_2(aq) + Cl_2(aq) \rightarrow 2FeCl_3(aq)$

(d) $2H_2O(l) + 2F_2(g) \rightarrow 4HF(aq) + O_2(g)$

(e) $I_2(aq) + SO_3^{2-}(aq) + H_2O(l) \rightarrow 2I^-(aq) + SO_4^{2-}(aq) + 2H^+(aq)$

3 Deduce the half-equations of oxidation and reduction for the following reactions:

(a) $Ca(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2(g)$

(b) $2Fe^{2+}(aq) + Cl_2(aq) \rightarrow 2Fe^{3+}(aq) + 2Cl^-(aq)$

(c) $Sn^{2+}(aq) + 2Fe^{3+}(aq) \rightarrow Sn^{4+}(aq) + 2Fe^{2+}(aq)$

(d) $Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$

4 Write balanced equations for the following reactions that occur in acidic solutions:

(a) $Zn(s) + SO_4^{2-}(aq) \rightarrow Zn^{2+}(aq) + SO_2(g)$

(b) $I^-(aq) + HSO_4^-(aq) \rightarrow I_2(aq) + SO_2(g)$

(c) $NO_3^-(aq) + Zn(s) \rightarrow NH_4^+(aq) + Zn^{2+}(aq)$

(d) $I_2(aq) + OCl^-(aq) \rightarrow IO_3^-(aq) + Cl^-(aq)$

(e) $MnO_4^-(aq) + H_2SO_3(aq) \rightarrow SO_4^{2-}(aq) + Mn^{2+}(aq)$

5 Which equation represents a redox reaction?

A $NaOH(aq) + HNO_3(aq) \rightarrow NaNO_3(aq) + H_2O(l)$

B $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

C $CuO(s) + 2HCl(aq) \rightarrow CuCl_2(aq) + H_2O(l)$

D $MgCO_3(s) + 2HNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + H_2O(l) + CO_2(g)$

6 The oxidation state of chromium is the same in all the following compounds except:

A $CrCl_3$ **B** Cr_2O_3 **C** $Cr_2(CO_3)_3$ **D** CrO_3

7 Deduce the names of the following compounds, using their oxidation numbers:

(a) Cr_2O_3 **(c)** HNO_3 **(d)** HNO_2 **(e)** PbO_2

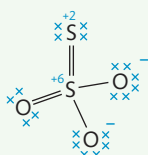**(b)** $CuCl$

NATURE OF SCIENCE

We have seen that oxidation states have several important uses as they enable us to:

- track redox changes in reactions;
- apply systematic names to compounds;
- determine reacting ratios in redox reactions.

At the same time, because they do not have a structural basis, oxidation states can raise some potential misunderstandings or ambiguities.

- Oxidation states do not distinguish between partial and complete transfer of electrons: +4 for C in CO_2 or +7 for Mn in $KMnO_4$ do not represent losses of 4 and 7 electrons respectively.
- In some cases, especially in organic chemistry, oxidation states have fractional values: in propane, C_3H_8, the oxidation state of C is $-2\frac{2}{3}$.
- Oxidation states and Lewis (electron dot) structures sometimes suggest conflicting information: CH_4, C_2H_6, and C_3H_8 are all similarly bonded molecules, but their C atoms have different oxidation states, −4, −3, and $-2\frac{2}{3}$ respectively.

In $S_2O_3^{2-}$, the rules would suggest oxidation states of +2 on each S atom, but from the Lewis

structure,   , values of +2 and +6 seem more appropriate.

Overall, oxidation states are best considered as a very useful tool that chemists use widely, while also keeping an eye on their limitations.

Oxidizing and reducing agents

We have seen that redox reactions *always* involve the simultaneous oxidation of one reactant with the reduction of another as electrons are transferred between them. The reactant that accepts electrons is called the **oxidizing agent** as it brings about oxidation of the other reactant. In the process it becomes reduced. Likewise the reactant that supplies the electrons is known as the **reducing agent**, because it brings about reduction and itself becomes oxidized. Sometimes the terms **reductant** and **oxidant** are used in place of reducing agent and oxidizing agent respectively.

Molten iron being tapped from a blast furnace for transfer to the steel-making furnace. Iron is extracted from its ore Fe_2O_3 by reducing it with carbon in the form of coke. Although blast furnaces existed in China from about the 5th century BCE and were widespread across Europe, a major development occurred in England in 1709. Substitution of the reducing agent charcoal for coke produced a less brittle form of iron. This accelerated the iron trade and was a key factor in the British Industrial Revolution.

For example, in the reaction where iron (Fe) is extracted from its ore (Fe_2O_3):

oxidizing   reducing
agent   agent

$$Fe_2O_3(s) \quad + \quad 3C(s) \quad \rightarrow \quad 2Fe(s) \quad + \quad 3CO(g)$$
$$\;+3 \qquad\qquad\; 0 \qquad\qquad\;\; 0 \qquad\qquad\; +2$$

(The oxidation state of O is not shown as it does not change during the reaction.)

The reducing agent C brings about the reduction of Fe ($+2 \rightarrow 0$), while it is oxidized to CO ($0 \rightarrow +2$). The oxidizing agent Fe_2O_3 brings about the oxidation of C, while itself is reduced to Fe.

Some examples of useful oxidizing and reducing agents are given below:

- oxidizing agent: O_2, O_3, H^+/MnO_4^-, $H^+/Cr_2O_7^{2-}$, F_2, Cl_2, conc. HNO_3, H_2O_2
- reducing agent: H_2, C, CO, SO_2, reactive metals

Note that whether a species acts as an oxidizing or as a reducing agent actually depends on what it is reacting with. For example, water can act as an oxidizing agent and be reduced to hydrogen, for example by sodium, or act as a reducing agent and be oxidized to oxygen, for example by fluorine.

- H_2O acting as an oxidizing agent:

$$2H_2O(l) + 2Na(s) \rightarrow 2NaOH(aq) + H_2(g)$$
$$+1 \qquad\qquad\qquad\qquad\qquad\qquad 0$$
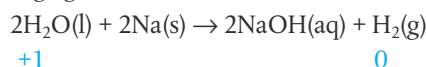
- H_2O acting as a reducing agent:

$$2H_2O(l) + 2F_2(g) \rightarrow 4HF(aq) + O_2(g)$$
$$-2 \qquad\qquad\qquad\qquad\qquad\qquad 0$$

In fact, water is weak both as an oxidizing agent and as a reducing agent, which is why it is such a useful solvent for many redox reactions.

Treatment of drinking water to kill pathogens commonly uses oxidizing agents such as chlorine and ozone. The process is effective and relatively cheap, yet millions of people worldwide lack access to clean drinking water. 'Access to safe water is a fundamental human need and therefore a human right.' Kofi Annan, United Nations Secretary General. In 2010 this human right was passed into international law, but this does not yet make it a reality for millions of people in developing countries.

More reactive metals are stronger reducing agents

Of course not all oxidizing and reducing agents are of equal strength. Some will be stronger than others, depending on their relative tendencies to lose or gain electrons. We learned in Chapter 4 that metals have a tendency to lose electrons and form positive ions, so they will act as reducing agents, pushing their electrons on to another substance. More reactive metals lose their electrons more readily and so we might expect that they will be stronger reducing agents than less reactive metals.

We can check this out by seeing if one metal is able to reduce the ions of another metal in solution. If we immerse zinc in a solution of copper sulfate, a reaction occurs. The blue colour of the solution fades, the pinkish-brown colour of copper metal appears and there is a rise in temperature. What is happening is that the Cu^{2+} ions are being displaced from solution as they are reduced by Zn. At the same time Zn dissolves as it is oxidized to Zn^{2+}.

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$

In a redox equation the substance that is reduced is the oxidizing agent, the substance that is oxidized is the reducing agent.
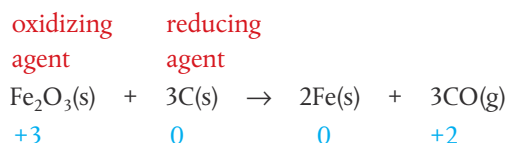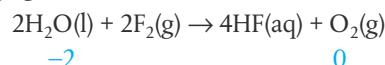
CHALLENGE YOURSELF

1 Hydrogen peroxide, H_2O_2, can also act as an oxidizing agent and as a reducing agent. With reference to the oxidation states of its atoms, suggest why this is so and which behaviour is more likely.

Single replacement reactions involving metals with metal ions

Full details of how to carry out this experiment with a worksheet are available online.
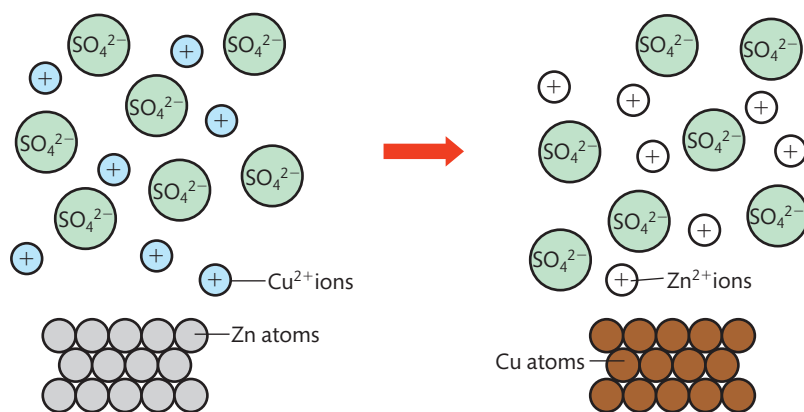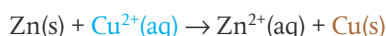
Figure 9.1 The reaction of zinc with copper(II) sulfate solution.

We can write this as an ionic equation without showing the sulfate ions as these act as spectator ions and are not changed during the reaction.

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

So zinc has acted as the reducing agent – it is therefore the more reactive metal. We can think of it as having the reducing strength to 'force' copper ions to accept the electrons.

We could confirm this by trying the reaction the other way round, with copper metal immersed in a solution of zinc ions. Can you predict what will happen? The answer is there will be no reaction, because Cu is not a strong enough reducing agent to reduce Zn^{2+}. This is another way of saying that it is a less reactive metal, less able to push the electrons onto Zn^{2+}.

By comparing **displacement** reactions like these between different combinations of metals and their ions, we can build up a list of relative strengths of the metals as reducing agents. This is called the **activity series** and it enables us to predict whether a particular redox reaction between a metal and the ions of another metal will be feasible. Later in this chapter we will learn how to quantify these differences in metal reactivity, which is of great importance in many industrial processes. For example, the extraction of a metal from its ore often involves choosing a suitable reducing agent by reference to these data.

Here is a small part of the activity series of metals:

Mg   strongest reducing agent, most readily becomes oxidized

Al

Zn

Fe

Pb

Cu

Ag   weakest reducing agent, least readily becomes oxidized

A simple activity series is given in section 25 of the IB data booklet and is not something that needs to be learned. The important thing is that you are able to interpret it and to deduce it from given data.
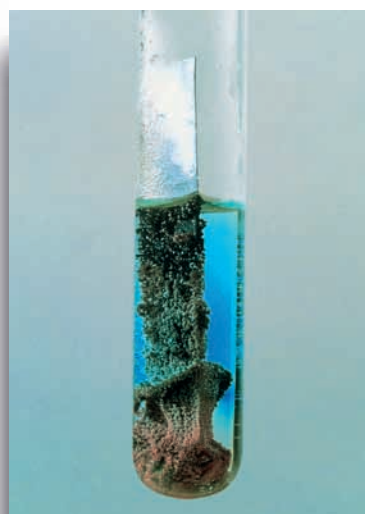
A strip of zinc metal half submerged in a solution of $CuSO_4$. Solid copper that appears brown is deposited and the blue colour fades as the copper ions are reduced by the zinc. Zinc is shown to be the stronger reducing agent.

More reactive metals are stronger reducing agents than less reactive metals.

A more reactive metal is able to reduce the ions of a less reactive metal.

Redox reactions between a metal and the oxide of a less reactive metal can also confirm the activity series. Here powdered aluminium reduces iron oxide, forming aluminium oxide and iron. $2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(s)$. This shows that aluminium is a stronger reducing agent than iron. The reaction is exothermic, creating short bursts of extremely high temperatures.

Worked example

Refer to the activity series given on page 417 to predict whether the following reactions will occur:

(a) $ZnCl_2(aq) + 2Ag(s) \rightarrow 2AgCl(s) + Zn(s)$

(b) $2FeCl_3(aq) + 3Mg(s) \rightarrow 3MgCl_2(aq) + 2Fe(s)$

Solution

(a) This reaction would involve Ag reducing Zn^{2+} in $ZnCl_2$. But Ag is a weaker reducing agent than Zn, so this will not occur.

(b) This reaction involves Mg reducing Fe^{3+} in $FeCl_3$. Mg is a stronger reducing agent than Fe, so this will occur.

We can investigate how some non-metals such as carbon and hydrogen would fit into this activity series of metals by similar types of displacement reactions. Carbon is able to reduce the oxides of iron and metals below it in the series, which provides one of the most effective means for the extraction of these metals. The position of hydrogen relative to the metals is discussed in section 19.1 on pages 432–435.

More reactive non-metals are stronger oxidizing agents

In a similar way, the different strengths of non-metals as oxidizing agents can be compared. For example, the halogens (Group 17 elements) react by gaining electrons and forming negative ions, and so act as oxidizing agents by removing electrons from other substances. We learned in Chapter 3 that their tendency to do this decreases down the group, so we would expect the following trend.

More reactive non-metals are stronger oxidizing agents than less reactive non-metals.

F	strongest oxidizing agent, most readily becomes reduced
Cl	
Br	
I	weakest oxidizing agent, least readily becomes reduced

Again this can be verified by reacting one halogen with solutions containing the ions of another halogen (known as halide ions). For example:

$$Cl_2(aq) + 2KI(aq) \rightarrow 2KCl(aq) + I_2(aq)$$
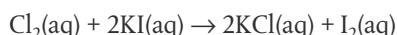
Here the Na^+ ions are spectator ions so we can write the ionic equation without showing them:

$$Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$$

The reaction occurs because Cl is a stronger oxidizing agent than I and so is able to remove electrons from it. In simple terms, you can think of it as a competition for electrons where the stronger oxidizing agent, in this case chlorine, will always 'win'.

Chlorine gas bubbling through a clear solution of potassium iodide KI. The solution is turning brown due to the formation of iodine in solution, as chlorine oxidizes the iodide ions and forms chloride ions.

Exercises

8 Identify the oxidizing agents and the reducing agents in the following reactions:

   (a) $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$
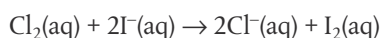   **(b)** $2Al(s) + 3PbCl_2(s) \rightarrow 2AlCl_3(s) + 3Pb(s)$
   (c) $Cl_2(aq) + 2KI(aq) \rightarrow 2KCl(aq) + I_2(aq)$
   (d) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

9 Use the two reactivity series given to predict whether reactions will occur between the following reactants, and write equations where relevant.

   (a) $CuCl_2 + Ag$ **(b)** $Fe(NO_3)_2 + Al$ **(c)** $NaI + Br_2$ **(d)** $KCl + I_2$

10 (a) Use the following reactions to deduce the order of reactivity of the elements W, X ,Y, Z, putting the most reactive first.

   $$W + X^+ \rightarrow W^+ + X \qquad\qquad X + Z^+ \rightarrow X^+ + Z$$
   $$Y^+ + Z \rightarrow \text{no reaction} \qquad\qquad X + Y^+ \rightarrow X^+ + Y$$

   (b) Which of the following reactions would you expect to occur according to the reactivity series you established in part (a)?
   (i) $W^+ + Y \rightarrow W + Y^+$
   (ii) $W^+ + Z \rightarrow W + Z^+$

> A more reactive non-metal is able to oxidize the ions of a less reactive non-metal.

Redox titrations

As with acid–base titrations (discussed in Chapter 8), redox titrations are used to determine the unknown concentration of a substance in solution. But in this case, the technique is based on a redox reaction between the two reactants, and finds the equivalence point where they have reacted stoichiometrically by transferring electrons. The two types of titration are compared below.

Acid–base titration	Redox titration
neutralization reaction between acid and base	redox reaction between oxidizing agent and reducing agent
protons are transferred from acid to base	electrons are transferred from reducing agent to oxidizing agent

Redox titrations are carried out in much the same way as acid–base titrations, using a burette and pipette to measure volumes accurately, and a standard solution of

one reactant. An indicator is usually used to signal the equivalence point, although some redox changes are accompanied by a colour change and may not need an external indicator. From the volume of the solution added from the burette to reach equivalence, which is known as the **titre**, the concentration of the other reactant can be determined. The calculations are based on the redox equation, which is typically developed from the half-equations.

Redox titrations are commonly used in the food and beverages industry, in the pharmaceutical industry, and in water and environmental analysis. For example, wines can be analysed for the presence of sulfur dioxide, and the vitamin C content of foods can be determined in this way. Some examples of common redox titrations that can be carried out in the laboratory are given below, and more details on how to carry out these experiments can be found online.

1 Analysis of iron with manganate(VII)

This redox titration uses $KMnO_4$ in an acidic solution as the oxidizing agent, which oxidizes Fe^{2+} ions to Fe^{3+}. During the reaction MnO_4^- is reduced to Mn^{2+}, so the overall equation is:

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$
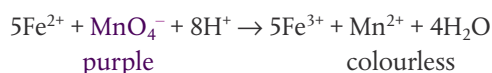
<div align="center">purple   colourless</div>

The reaction is accompanied by a colour change from deep purple to colourless, so the reaction acts as its own indicator, signalling the equivalence point.

Worked example

All the iron in a 2.000 g tablet was dissolved in an acidic solution and converted to Fe^{2+}. This was then titrated with $KMnO_4$. The titration required 27.50 cm^3 of 0.100 mol dm^{-3} $KMnO_4$. Calculate the total mass of iron in the tablet and its percentage by mass. Describe what would be observed during the reaction, and how the equivalence point can be detected.

Solution

First we need the balanced equation for the reaction, which is solved by the half-equation method described earlier.

    oxidation: $Fe^{2+} \rightarrow Fe^{3+} + e^-$

    reduction: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

    overall: $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$
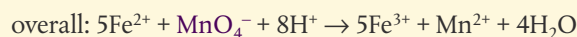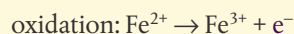
Next we need to know the amounts of reactants used to reach equivalence. We start with $KMnO_4$ as we know both its concentration and its volume.

$$n = cV$$

$$n(MnO_4^-) = 0.100 \text{ mol dm}^{-3} \times \frac{27.50}{1000} \text{ dm}^3 = 0.00275 \text{ mol MnO}_4^-$$

From the equation for the reaction we know the reacting ratio:

$MnO_4^- : Fe^{2+} = 1 : 5$
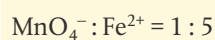
$\therefore$ mol $Fe^{2+} = 0.00275$ mol $MnO_4^- \times 5 = 0.01375$ mol

The browning of fruit when it is exposed to the air is an oxidation reaction. It occurs when phenols released in damaged cells are oxidized with molecular oxygen at alkaline pH. The brown products are tannins. Food chemists are often interested in slowing down these reactions using reducing agents such as SO_2 or vitamin C, for example in lemon juice.

Redox titration
Full details of how to carry out this experiment with a worksheet are available online.

$M(Fe) = 55.85$ g mol^{-1}

$$n = \frac{m}{M}$$

$\therefore$ $m(Fe) = 0.01375$ mol $\times 55.85$ g mol$^{-1} = 0.7679$ g

% Fe in tablet $= \dfrac{0.768 \text{ g}}{2.000 \text{ g}} \times 100 = 38.39\%$

$\therefore$ Fe in tablet $= 0.768$ g, 38.4%

MnO_4^- in the burette is purple, but forms a nearly colourless solution in the flask as it reacts to form Mn^{2+}. But when the reducing agent Fe^{2+} in the flask has been used up at equivalence, MnO_4^- ions will not react and the purple colour will persist.

2 Iodine–thiosulfate reaction

Several different redox titrations use an oxidizing agent to react with excess iodide ions to form iodine.

$$2I^-(aq) + \text{oxidizing agent} \rightarrow I_2(aq) + \text{reduced product}$$

Examples of oxidizing agents used in this way include $KMnO_4$, KIO_3, $K_2Cr_2O_7$, and $NaOCl$.

The liberated iodine, I_2, is then titrated with sodium thiosulfate, $Na_2S_2O_3$, using starch as an indicator.

Redox equations:

oxidation: $2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$

reduction: $I_2 + 2e^- \rightarrow 2I^-$

The overall equation is:

$$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$
<div align="center">deep blue in
presence of starch</div>
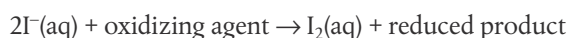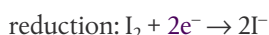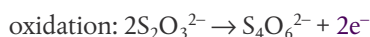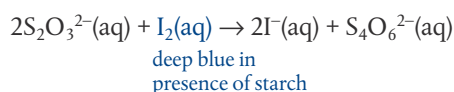
The starch indicator is added during the titration (not at the start) and forms a deep blue colour by forming a complex with free I_2. As the I_2 is reduced to I^- during the reaction, the blue colour disappears, marking the equivalence point.

amylose helix, a polymer of glucose and an important component of starch

I_3^-
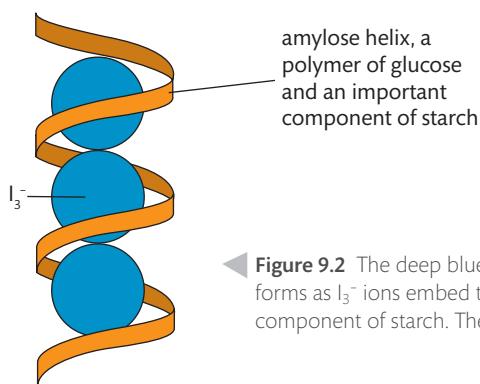
Figure 9.2 The deep blue complex between iodine solution and starch forms as I_3^- ions embed themselves within the helix of amylose, a component of starch. The structure of I_3^- was discussed in Chapter 4.

Because iodine, I_2, has a very low solubility in water, it is used instead in the form of 'iodine solution', which is made by dissolving I_2 in iodide ions, forming the complex ion $I_3^-(aq)$. It is the I_3^- ion that gives the deep blue complex with starch. Even though I_3^- is the reactant, it is still valid to use I_2 in the equations, as this is the 'active ingredient'. Technically, starch is not a redox indicator as such, as it responds to the disappearance of I_2, rather than to a change in the redox potential of the solution.

CHALLENGE YOURSELF

3 From your knowledge of the structure of I_3^-, consider why it forms a stable complex in the hydrophobic interior of the amylose helix.

Worked example

Household bleach is an oxidizing agent that contains sodium hypochlorite, NaOCl, as the active ingredient. It reacts with iodide ions in acidic solution as follows:

$$OCl^-(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + Cl^-(aq) + H_2O(l)$$
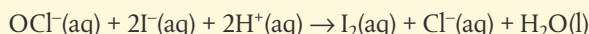
A 10.00 cm³ sample of bleach was reacted with a solution of excess iodide ions, and the liberated iodine was then titrated with $Na_2S_2O_3$. The titration required 38.65 cm³ of 0.0200 mol dm⁻³ $Na_2S_2O_3$. Determine the concentration of OCl^- in the bleach.

Solution

First we need the balanced equation for the titration, which is solved by the half-equation method on page 413.

$$2Na_2S_2O_3(aq) + I_2(aq) \rightarrow 2NaI(aq) + Na_2S_4O_6(aq)$$
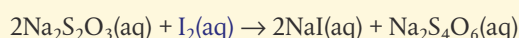
Next we calculate the number of moles of $Na_2S_2O_3$ as we know both its concentration and its volume.

$$n = cV$$

$$n(S_2O_3^{2-}) = 0.0200 \text{ mol dm}^{-3} \times \frac{38.65}{1000} \text{ dm}^3 = 7.73 \times 10^{-4} \text{ mol S}_2O_3^{2-}$$

From the equation for the reaction we know the reacting ratio

$$S_2O_3^{2-} : I_2 = 2 : 1$$
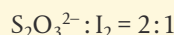
$$\therefore \text{ mol I}_2 = 7.73 \times 10^{-4} \times 0.5 = 3.865 \times 10^{-4}$$

This is a back-titration as the I_2 was liberated by the reaction of I^- with OCl^-, as given in the question. The reacting ratio is

$$OCl^-(aq) : I_2(aq) = 1 : 1$$
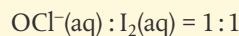
$$\therefore \text{ mol OCl}^- = \text{mol I}_2 = 3.865 \times 10^{-4}$$

The concentration of the OCl^- in the bleach can now be calculated.

$$n(OCl^-) = cV$$

$$\therefore 3.865 \times 10^{-4} \text{ mol} = c \times \frac{10.00}{1000} \text{ dm}^3$$

$$[OCl^-] = 0.0387 \text{ mol dm}^{-3}$$

A canal in England covered in a bloom of duckweed. This is an aquatic weed that thrives in water that contains pollutants such as phosphates. This is known as eutrophication. The bloom blocks out sunlight to deeper layers of the water ecosystem, and so lowers the level of dissolved oxygen.

3 Winkler method for calculating dissolved oxygen

The **dissolved oxygen** content of water is one of the most important indicators of its quality, as oxygen is essential to the survival of aquatic life. As the level of pollution in water increases, the dissolved oxygen content generally decreases, as the oxygen is used by bacteria in decomposition reactions. The **biological oxygen demand** (BOD) is therefore used as a means of measuring the degree of pollution. BOD is defined as the amount of oxygen used to decompose the organic matter in a sample of water over a specified

time period, usually five days at a specified temperature. A high BOD indicates a greater quantity of degradable organic waste in the water, which means a lower level of dissolved oxygen.

Redox titrations can be used to measure the dissolved oxygen in water, and from this calculate the BOD in a process known as the **Winkler method**. The principle is based on a sequence of redox reactions as follows.

1   The dissolved oxygen, $O_2(g)$, in the water is 'fixed' by the addition of a manganese(II) salt such as $MnSO_4$. Reaction of this salt with O_2 in basic solution causes oxidation of Mn(II) to higher oxidation states, such as Mn(IV):

$$2Mn^{2+}(aq) + O_2(g) + 4OH^-(aq) \rightarrow 2MnO_2(s) + 2H_2O(l)$$
$$\quad +2 \qquad\qquad\qquad\qquad\qquad\qquad +4$$

2   Acidified iodide ions, I^-, are added to the solution, and are oxidized by the Mn(IV) to I_2:

$$MnO_2(s) + 2I^-(aq) + 4H^+(aq) \rightarrow Mn^{2+}(aq) + I_2(aq) + 2H_2O(l)$$
$$\quad +4 \qquad\qquad\qquad\qquad\qquad\qquad +2$$

3   The iodine produced is then titrated with sodium thiosulfate, as described earlier:

$$2S_2O_3{}^{2-}(aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6{}^{2-}(aq)$$

So we can see that in the overall sequence, for every 1 mole of O_2 in the water, 4 mol of $S_2O_3{}^{2-}$ are used.

Worked example

A 500 cm³ sample of water was collected and tested for dissolved oxygen by the addition of $MnSO_4$ in basic solution, followed by the addition of acidified KI. It was found that 12.50 cm³ of 0.0500 mol dm⁻³ $Na_2S_2O_3(aq)$ was required to react with the iodine produced. Calculate the dissolved oxygen content of the water in g dm⁻³, using the equations given above.

Solution

Start with calculating the amount of $S_2O_3{}^{2-}$, as we are given both its volume and its concentration.

$$n = cV$$

$$n(S_2O_3{}^{2-}) = 0.0500 \text{ mol dm}^{-3} \times \frac{12.50}{1000} \text{ dm}^3 = 6.25 \times 10^{-4} \text{ mol}$$

From the reacting ratio in step 3, $S_2O_3{}^{2-} : I_2 = 2 : 1$

$$\therefore n(I_2) = 0.5 \times 6.25 \times 10^{-4} = 3.175 \times 10^{-4} \text{ mol}$$

BOD is the quantity of oxygen needed to oxidize organic matter in a sample of water over a five-day period at a specified temperature.

CHALLENGE YOURSELF

4   How would you expect the dissolved oxygen content of a lake to be affected by discharge of hot water from an industrial site? Explain why this effect occurs.

From the reacting ratio in step 2, $I_2 : MnO_2 = 1 : 1$

$\therefore n(MnO_2) = 3.175 \times 10^{-4}$ mol

From the reacting ratio in step 1, $MnO_2 : O_2(g) = 2 : 1$

$\therefore n(O_2) = 0.5 \times 3.175 \times 10^{-4}$ mol $= 1.5875 \times 10^{-4}$ mol

(We could also go directly from a ratio of $O_2 : S_2O_3^{2-} = 1 : 4$)

Finally express the amount of $O_2(g)$ as g dm^{-3}

$\qquad m(O_2) = n \times M = 1.5875 \times 10^{-4}$ mol $\times 32.00$ g mol$^{-1} = 5.080 \times 10^{-3}$ g in 500 cm^3

$\therefore$ dissolved oxygen $= 0.0102$ g dm^{-3}

NATURE OF SCIENCE

We have seen that oxidation and reduction can be defined in different ways, and that these different definitions do not contradict but are consistent with each other. Which definition we choose to apply will be determined by the particular example, and by which approach gives the simplest, most useful interpretation of the type of reaction occurring.

Oxidation	Reduction
gain of oxygen	loss of oxygen
loss of hydrogen	gain of hydrogen
loss of electrons	gain of electrons
increase in oxidation state	decrease in oxidation state
brought about by an oxidizing agent that becomes reduced	brought about by a reducing agent that becomes oxidized

We have seen similar situations earlier in this text where different theories used to describe the same phenomenon persist. Sometimes the theories are distinct, such as the particle–wave theories of electron behaviour, at other times, one represents a broader generalization of the other, such as the distinction between Brønsted–Lowry and Lewis acid–base behaviour. As long as a theory leads to testable predictions and can be supported by experimental data, it has validity and contributes to the understanding of the phenomenon.

Exercises

11 A bag of 'road salt', used to melt ice and snow from roads, contains a mixture of calcium chloride, $CaCl_2$, and sodium chloride, NaCl. A 2.765 g sample of the mixture was analysed by first converting all the calcium into calcium oxalate, CaC_2O_4. This was then dissolved in H_2SO_4, and titrated with 0.100 mol dm^{-3} $KMnO_4$ solution. The titration required 24.65 cm^3 of $KMnO_4$(aq) and produced Mn^{2+}(aq), CO_2(g), and H_2O(l).

  (a) What would be observed at the equivalence point of the titration?
  (b) Write the half-equation for the oxidation reaction, starting with $C_2O_4^{2-}$.
  (c) Write the half-equation for the reduction reaction, starting with MnO_4^-.
  (d) Write the overall equation for the redox reaction.
  (e) Determine the number of moles of $C_2O_4^{2-}$.
  (f) Deduce the number of moles of Ca^{2+} in the original sample.
  (g) What was the percentage by mass of $CaCl_2$ in the road salt?

12 Alcohol levels in blood can be determined by a redox titration with potassium dichromate, $K_2Cr_2O_7$, according to the following equation.

$$C_2H_5OH(aq) + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \rightarrow 2CO_2(g) + 4Cr^{3+}(aq) + 11H_2O(l)$$

  (a) Determine the alcohol percentage in the blood by mass if a 10.000 g sample of blood requires 9.25 cm^3 of 0.0550 mol dm^{-3} $K_2Cr_2O_7$ solution to reach equivalence.
  (b) Describe the change in colour that would be observed during the titration.

9.2 & 19.1 Electrochemical cells

Understandings:

Voltaic (Galvanic) cells

- Voltaic cells convert energy from spontaneous, exothermic chemical processes to electrical energy.
- Oxidation occurs at the anode (negative electrode) and reduction occurs at the cathode (positive electrode) in a voltaic cell.
- A voltaic cell generates an electromotive force (EMF) resulting in the movement of electrons from the anode (negative electrode) to the cathode (positive electrode) via the external circuit. The EMF is termed the cell potential ($E^\ominus$).
- The standard hydrogen electrode (SHE) consists of an inert platinum electrode in contact with 1 mol dm^{-3} hydrogen ion and hydrogen gas at 100 kPa and 298 K. The standard electrode potential ($E^\ominus$) is the potential (voltage) of the reduction half-equation under standard conditions measured relative to the SHE. Solute concentration is 1 mol dm^{-3} or 100 kPa for gases. $E^\ominus$ of the SHE is 0 V.
- $G^\ominus = -nFE^\ominus$. When $E^\ominus$ is positive, $\Delta G^\ominus$ is negative indicative of a spontaneous process. When $E^\ominus$ is negative, $\Delta G^\ominus$ is positive indicative of a non-spontaneous process. When $E^\ominus$ is 0, then $\Delta G^\ominus$ 0.

  ### Guidance
  - $\Delta G^\ominus = -nFE^\ominus$ *is given in the data booklet in section 1.*
  - *Faraday's constant* = 96 500 C mol^{-1} *is given in the data booklet in section 2.*

Electrolytic cells

- Electrolytic cells convert electrical energy to chemical energy, by bringing about non-spontaneous processes.
- Oxidation occurs at the anode (positive electrode) and reduction occurs at the cathode (negative electrode) in an electrolytic cell.
- When aqueous solutions are electrolysed, water can be oxidized to oxygen at the anode and reduced to hydrogen at the cathode.
- Current, duration of electrolysis, and charge on the ion affect the amount of product formed at the electrodes during electrolysis.

  ### Guidance
  Electrolytic processes to be covered in theory should include the electrolysis of aqueous solutions (e.g. sodium chloride, copper(II) sulfate, etc.) and water using both inert platinum or graphite electrodes and copper electrodes.

- Electroplating involves the electrolytic coating of an object with a metallic thin layer.

  ### Guidance
  The term cells in series should be understood.

Applications and skills:

- Construction and annotation of both types of electrochemical cells.

  ### Guidance
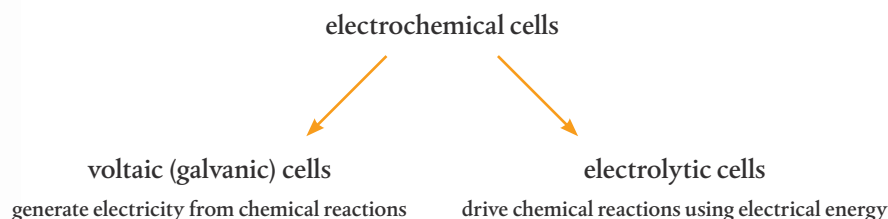 *For voltaic cells, a cell diagram convention should be covered.*

- Explanation of how a redox reaction is used to produce electricity in a voltaic cell and how current is conducted in an electrolytic cell.
- Distinction between electron and ion flow in both electrochemical cells.
- Performance of laboratory experiments involving a typical voltaic cell using two metal/metal-ion half-cells.
- Deduction of the products of the electrolysis of a molten salt.

  ### Guidance
  Explanations should refer to $E^\ominus$ values, nature of the electrode, and concentration of the electrolyte.

- Calculation of cell potentials using standard electrode potentials.
- Prediction of whether a reaction is spontaneous or not using $E^\ominus$ values.
- Determination of standard free-energy changes ($\Delta G^\ominus$) using standard electrode potentials.
- Explanation of the products formed during the electrolysis of aqueous solutions.
- Perform lab experiments that could include single replacement reactions in aqueous solutions.
- Determination of the relative amounts of products formed during electrolytic processes.
- Explanation of the process of electroplating.

The fact that redox reactions involve transfers of electrons immediately suggests a link between this type of chemical reactivity and electricity. The main applications of this are collectively known as **electrochemical cells**, of which there are two main types.

electrochemical cells

voltaic (galvanic) cells
generate electricity from chemical reactions

electrolytic cells
drive chemical reactions using electrical energy

We will consider each of these types of cell in turn.

Voltaic cells
Voltaic cells generate electricity from spontaneous redox reactions

Building voltaic cells with different combinations of metals/metal ion electrodes will help in the understanding of this topic. Full details with a worksheet are available online.

Let us consider again the reaction we discussed on pages 416–417 in which zinc reduced copper ions. Remember that here zinc was the reducing agent and became oxidized while copper ions were reduced. When the reaction is carried out in a single test tube, as shown in the photo on page 417, the electrons flow spontaneously from the zinc to the copper ions in the solution, and as we noted, energy is released in the form of heat as it is an exothermic reaction. There is, however, a different way of organizing this reaction so that the energy released in the redox reaction, instead of being lost as heat, is available as electrical energy. It is really just a case of separating the two half-reactions

oxidation $\quad$ $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ and

reduction $\quad$ $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
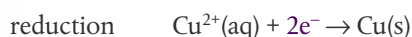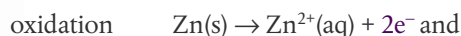
into so-called **half-cells**, and allowing the electrons to flow between them only through an external circuit. This is known as a **voltaic** or a **galvanic cell**, and we will see how it is constructed in the next section.

Half-cells generate electrode potentials

There are many types of half-cell but probably the simplest is made by putting a strip of metal into a solution of its ions.
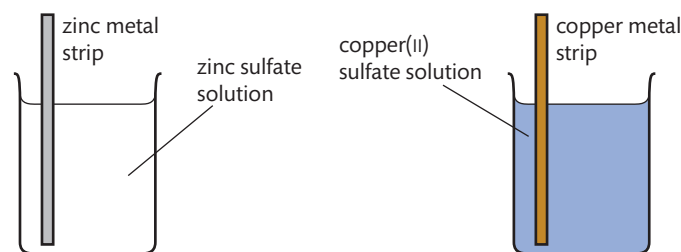
A copper half-cell consisting of a piece of copper metal dipping into a solution of a copper salt. An equilibrium is set up between the Cu metal and its ions:
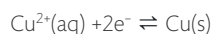
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$

Figure 9.3 Copper and zinc half-cells.

zinc metal strip

zinc sulfate solution

copper(II) sulfate solution

copper metal strip

In the zinc half-cell, zinc atoms will form ions by releasing electrons that will make the surface of the metal negatively charged with respect to the solution.
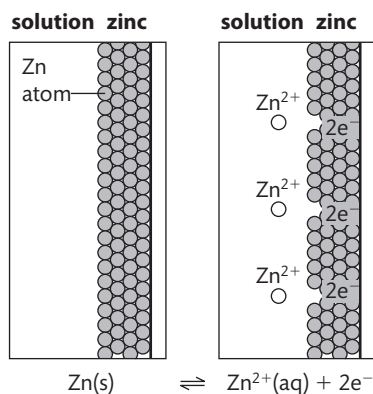

$$Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$$

Figure 9.4 Zinc atoms form zinc ions by releasing electrons. An equilibrium is set up between the metal and its solution of ions.

There will therefore be a charge separation, known as an **electrode potential**, between the metal and its ions in solution. At the same time, ions in the solution gain electrons to form Zn atoms, so an equilibrium exists as follows:

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$$
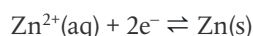
The position of this equilibrium determines the size of the electrode potential in the half-cell, and depends on the reactivity of the metal.

Because copper is the less reactive metal, in its half-cell the equilibrium position for the equivalent reaction:

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$$
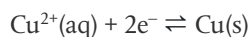
lies further to the right. In other words, copper has less of a tendency to lose electrons than zinc. Consequently, there are fewer electrons on the copper metal strip, so it will develop a higher (or less negative) electrode potential than the zinc half-cell.

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$$
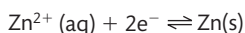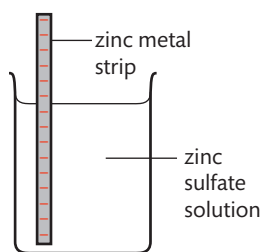
Some zinc atoms from the metal strip release electrons, giving it a negative charge.

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$$
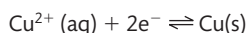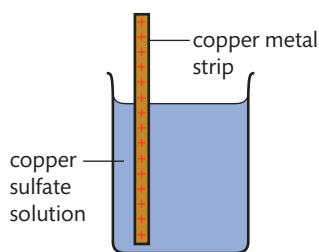
Some copper ions in the solution accept electrons from the copper rod giving it a positive charge.

Figure 9.5 The zinc half-cell develops a negative potential with respect to the copper half-cell.

The equilibrium as written for the copper half-cell lies further to the right than the equilibrium in the zinc half-cell.

In general the more reactive a metal, the more negative its electrode potential in its half-cell.

Two connected half-cells make a voltaic cell

If we now connect these two half-cells by an external wire, electrons will have a tendency to flow spontaneously from the zinc half-cell to the copper half-cell because of their different electrode potentials. The half-cells connected in this way are often

called **electrodes**, and their name gives us information about the type of reaction that occurs there. The electrode where oxidation occurs is called the **anode**, in this case it is the zinc electrode and it has a negative charge:

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

The electrode where reduction occurs is called the **cathode**, in this case it is the copper electrode and it has a positive charge:

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

A potential difference will, however, only be generated between the electrodes when the circuit is complete.

> Oxidation always occurs at the anode; reduction always occurs at the cathode. In the voltaic cell, the anode has a negative charge and the cathode has a positive charge.

Figure 9.6 This cell has an incomplete circuit – no voltage is generated. A salt bridge must be added to allow ions to flow between the two electrodes.
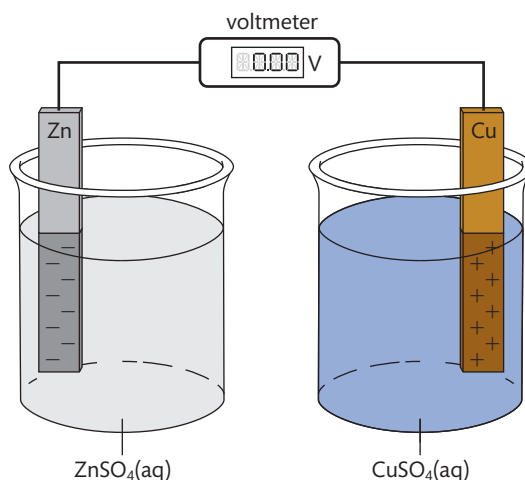
The voltaic cell therefore must have the following connections between the half-cells.

- An external electronic circuit, connected to the metal electrode in each half-cell. A voltmeter can also be attached to this external circuit to record the voltage generated. Electrons will flow from the anode to the cathode through the wire.
- A salt bridge completes the circuit. The salt bridge is a glass tube or strip of absorptive paper that contains an aqueous solution of ions. Movement of these ions neutralizes any build-up of charge and maintains the potential difference. Anions move in the salt bridge from the cathode to the anode, which opposes the flow of electrons in the external circuit. Cations move in the salt bridge from the anode to the cathode. The

Zinc–copper voltaic cell showing a copper half-cell and a zinc half-cell connected by a salt bridge that appears white. Electrons flow from the zinc electrode to the copper electrode through the electrical wires, while ions flow through the salt bridge to complete the circuit. The voltmeter is showing 1.10 V, the potential difference of this cell.

solution chosen is often aqueous $NaNO_3$ or KNO_3 as these ions will not interfere with the reactions at the electrodes. Without a salt bridge, no voltage is generated.
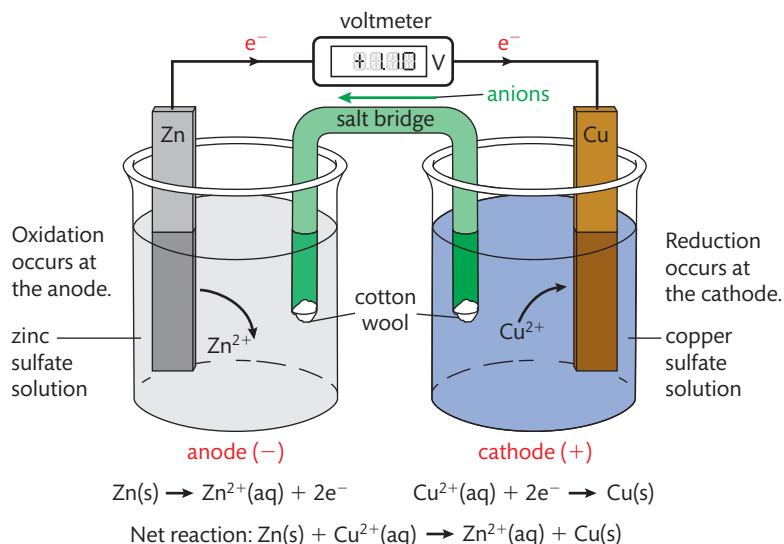

Figure 9.7 A copper–zinc voltaic cell.

anode (−)   cathode (+)

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

Net reaction: $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

You may be familiar with the sensation of a mild electric shock when you happen to bite some aluminium foil on a tooth that has a filling. The filling is made of an amalgam of mercury and either tin or silver, and creates a voltaic cell when it touches the foil. Aluminium is the anode, the filling is the cathode, and the saliva is the electrolyte 'salt bridge'. A weak current flows between the electrodes and is detected by the sensitive nerves in the teeth.

A voltaic cell converts the energy released from a spontaneous, exothermic reaction into electrical energy.

Cell diagram convention

Rather than always drawing out all the components of a voltaic cell, a shorthand version known as a **cell diagram convention** can be used. This has the following features:

- a single vertical line represents a phase boundary such as that between a solid electrode and an aqueous solution within a half-cell;
- a double vertical line represents the salt bridge;
- the aqueous solutions of each electrode are placed next to the salt bridge;
- the anode is generally put on the left and the cathode on the right, so electrons flow from left to right;
- spectator ions are usually omitted from the diagram;
- if a half-cell includes two ions, they are separated by a comma because they are in the same phase (see page 434).

The cell diagram convention is shown below for the copper–zinc cell.

salt bridge   phase boundary

$Zn(s) \,|\, Zn^{2+}(aq) \,\|\, Cu^{2+}(aq) \,|\, Cu(s)$

anode   cathode
oxidation   reduction

electrons flow this way
via external circuit

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
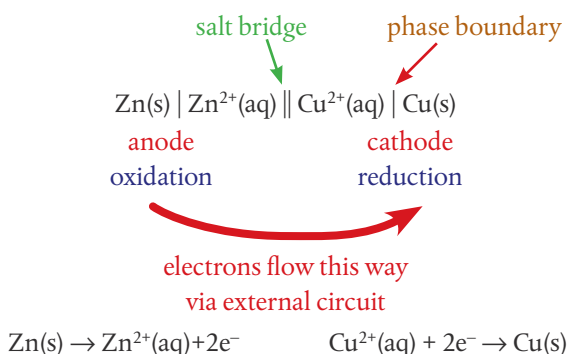
The placing of the anode and cathode on the left and right is not universally used. The important thing is that the diagram is clearly labelled and leads to the correct interpretation of the direction of electron flow and the interpretation of $E^{\ominus}$ data as described in the next section.
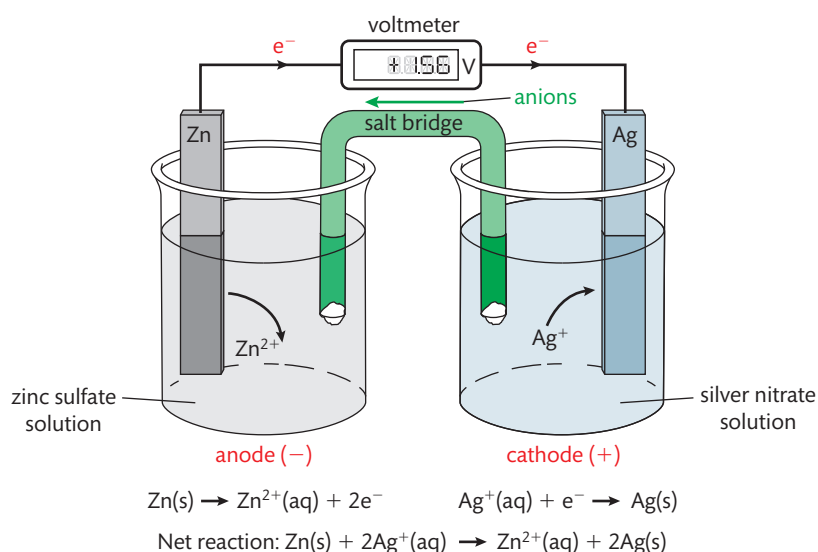
Different half-cells make voltaic cells with different voltages

Any two half-cells can be connected together similarly to make a voltaic cell. For any such cell the direction of electron flow and the voltage generated will be determined by the *difference* in reducing strength of the two metals. In most cases this can be judged by the relative position of the metals in the reactivity series. For example if we changed the copper half-cell in the example above to a silver half-cell, a larger voltage would be produced because the difference in electrode potentials of zinc and silver is greater than between that of zinc and copper. Electrons would flow from zinc (anode) to silver (cathode), as shown in Figure 9.8.

Figure 9.8 A silver–zinc voltaic cell.

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \qquad Ag^+(aq) + e^- \longrightarrow Ag(s)$$

Net reaction: $Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$

Electrons always flow in the external circuit from anode to cathode.

If we now make a voltaic cell with one copper electrode and one silver electrode, the direction of electron flow would be *away* from copper towards silver. In other words, copper will be the anode and silver the cathode. This is due to the greater reducing power of copper – it has the lower electrode potential.
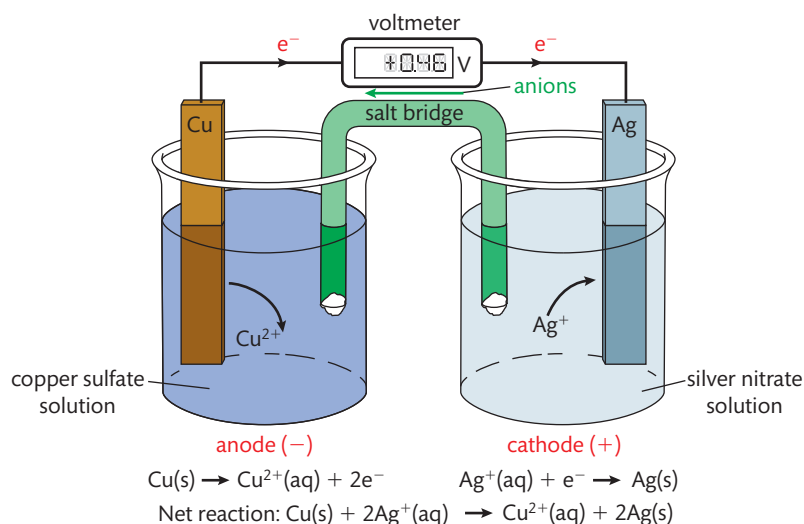

Figure 9.9 A silver–copper voltaic cell.

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

Net reaction: $Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$

We can now summarize the parts of a voltaic cell and the direction of movement of electrons and ions:

- electrons flow from anode to cathode through the external circuit;
- anions migrate from cathode to anode through the salt bridge;
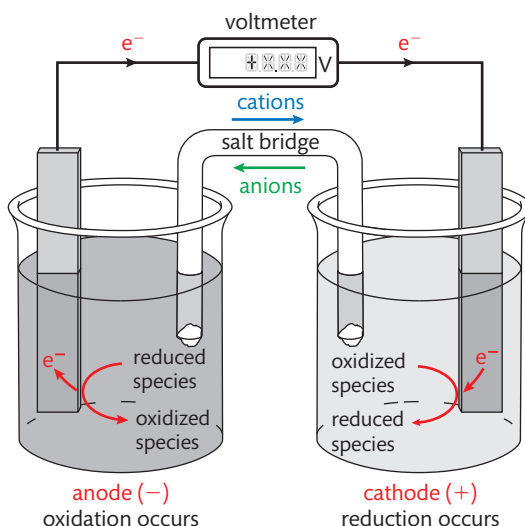- cations migrate from anode to cathode through the salt bridge.

▲
USB batteries. These rechargeable batteries are charged by plugging them into the USB port of a computer.

Batteries are an application of a voltaic cell, making electrical energy available as a source of power. Our reliance on batteries increases as global demand for mobile electronic devices such as smart phones, laptops, and tablets continues to grow. China is the largest market, while India and South Korea are growing the fastest. The largest growth is in the area of rechargeable batteries, with estimates placing the global market up to 100 billion US dollars. While demand for batteries looks set to continue, concern over toxicity and environmental damage from battery disposal has meant that mercury and cadmium batteries are being phased out in many places. The different types of batteries and their relative advantages are explained more fully in Option C, Energy.

Exercises

13 Use the metal reactivity series in section 25 of the IB data booklet to predict which electrode will be the anode and which will be the cathode when the following half-cells are connected. Write half-equations for the reactions occurring at each electrode.

  (a) Zn/Zn^{2+} and Fe/Fe^{2+}
  (b) Fe/Fe^{2+} and Mg/Mg^{2+}
  (c) Mg/Mg^{2+} and Cu/Cu^{2+}

14 (a) Draw a voltaic cell with one half-cell consisting of Mg and a solution of Mg^{2+} ions and the other consisting of Zn and a solution of Zn^{2+} ions. Label the electrodes with name and charge, the direction of electron and ion movement, and write equations for the reactions occurring at each electrode.

  (b) Draw a cell diagram to represent the above voltaic cell.

15 Predict what would happen if an iron spatula was left in a solution of copper sulfate overnight.

INVENTIONS ILLUSTRES
La pile de Volta

Italian physicist Count Alessandro Volta (1745–1827) demonstrates his newly-invented battery or 'voltaic pile' to Napoleon Bonaparte in 1801. Constructed from alternating discs of zinc and copper with pieces of cardboard soaked in brine between the metals, his voltaic pile was the first battery that produced a reliable, steady current of electricity.

The first observations of the link between electricity and chemical change are usually credited to the Italian scientist Luigi Galvani in 1791. He discovered what he called 'animal electricity' by accident, when he noticed twitching in the leg muscles of a dead frog when it was in contact with two different metals. After many experiments, he concluded that the contractions were caused by an electrical fluid that was carried to the muscles in the nerves. His contemporary and fellow countryman Alessandro Volta, however, had an intuition that the source of the electricity was not biological, but originated instead from the interaction between two metals. He set out to prove it by building a 'voltaic pile' from pairs of metals separated by a conducting solution, and demonstrated that this generated an electric current. The fact that the terms galvanic cell and voltaic cell are still both used reflects the recognition given to both men in the discovery.

The invention of the battery shows how a chance observation, followed by experimentation, debate, and the testing of hypotheses led to the development of theory with testable predictions which is then supported by evidence.

Standard electrode potentials

Quick reference of units and terms used in electrochemistry

Here are some definitions of terms used in electrochemistry and an introduction to the units used.

- The SI unit of electric current (I) is the **ampere**, usually known as **amp** (**A**). It is an SI base unit, from which other units are derived.
- The SI unit of electric charge (Q) is the **coulomb** (**C**). It is the amount of charge transported in 1 second by a current of 1 ampere. The charge on a single electron is 1.602×10^{-19} C, so one mole of electrons carries a charge of 96485.34 C mol^{-1}, known as a **faraday** (**F**).

  So the familiar equation $Q = I \times t$ can also be written as C = A $\times$ s

  The charge on a single electron is 1.602×10^{-19} C, so 1 mol of electrons carries a charge of 96 485.34 C mol^{-1}.
- The SI unit of potential difference is the **volt** (**V**). It is equal to the difference in electric potential between two points on a conducting wire, and defined as the amount of energy (J) that can be delivered by a coulomb of electric charge (C). $V = J \times C^{-1}$
- The **electromotive force** (**EMF**) of a cell is the greatest potential difference that it can generate. It is measured in volts. In practice, because of its internal resistance, it is measurable only when the cell is not supplying current. We will use the term **cell potential** E_{cell} to describe the potential difference when generating electrical energy.
- Cells in series are connected along the same path, so the same current flows through all components.

Comparisons of half-cell electrode potentials need a reference point

A voltaic cell generates a potential difference known as the **electromotive force** (**EMF**). As electrons tend to flow from the half-cell with the more negative potential to the half-cell with the more positive potential, the potential generated is called the **cell potential** or **electrode potential** and is given the symbol **E**. The magnitude of this voltage depends on the *difference* in the tendencies of these two half-cells to undergo reduction. Clearly, the electrode potential of a single half-cell cannot be measured in isolation, but only when electrons flow as it is linked in this way to another half-cell. Therefore, in order to draw up a list of the relative reducing power of different half-cells, it is necessary to compare them all with some fixed reference point that acts as

a standard for measurement. It is similar to the way in which heights of mountains can be compared with each other because each is given a height relative to an agreed zero point, in this case sea level.

In electrochemistry, the reference standard is the **standard hydrogen electrode**, sometimes known as **SHE**. As we will see, this gives us a baseline for measuring and comparing the electrode potentials of other half-cells.

The standard hydrogen electrode

The standard hydrogen electrode (sometimes called the standard hydrogen half-cell) is a modified form of the pH electrode encountered in Chapter 8.

$H_2(g)$ at 298 K and 100 kPa

platinum electrode

glass tube with holes in to allow bubbles of $H_2(g)$ to escape

acid solution containing 1.0 mol dm^{-3} $H^+(aq)$
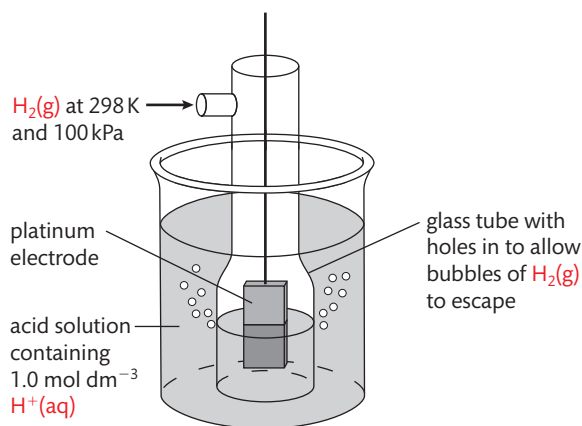
Figure 9.11 The standard hydrogen electrode (SHE).

> Do not confuse *absorption* with *adsorption*. Absorption occurs when something is taken up through the *volume* of another substance, such as a sponge taking up water; adsorption occurs only at the *surface*, and so depends on the surface area.

Platinum is used as the conducting metal in the electrode because it is fairly inert and will not ionize, and it also acts as a catalyst for the reaction of proton reduction. It is used in the form of 'platinized platinum', which means the surface of the metal is coated with very finely divided platinum (sometime known as platinum black). This causes the electrode reaction to happen rapidly as the large surface area helps in the adsorption of hydrogen gas. Note that the concentration of $H^+(aq)$ is 1.0 mol dm^{-3} (pH = 0) and the pressure of $H_2(g)$ is 100 kPa at 298 K.

As the electrode is immersed in the acidic solution, it is alternately bathed in $H^+(aq)$ and $H_2(g)$, setting up an equilibrium between the adsorbed layer of $H_2(g)$ and aqueous H^+ ions.

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$
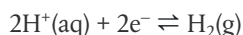
The reaction is reversible, occurring as reduction of H^+ (forward reaction) or as oxidation of H_2 (backward reaction), depending on the electrode potential of the half-cell to which it is linked, as we will see below.

The hydrogen half-cell is arbitrarily assigned an electrode potential of zero volts, 0 V. This gives us a means to measure and compare electrode potentials of any other half-cell to which it is connected.

> The standard hydrogen electrode is assigned an electrode potential value of 0 V.

NATURE OF SCIENCE

The standard electrode potential concept brings a quantitative approach to the study of electrochemistry. As there is no absolute reference point, a convenient reference standard is chosen, in much the same way as we saw with entropy in Chapter 5. This lends itself to mathematical analysis and enables scientists to recognize patterns, trends, and discrepancies.
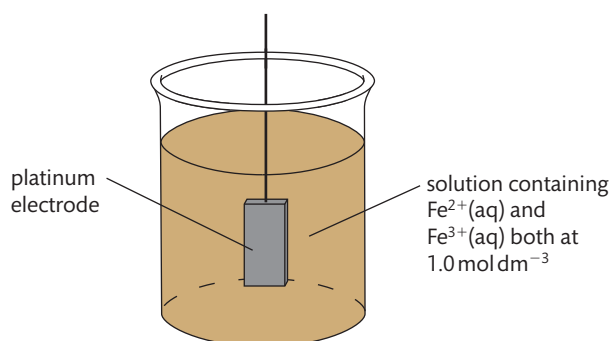
Measuring standard electrode potentials

As electrode potentials depend on the concentrations of ions, gas pressures, purity of substance, and temperature, these must all be controlled in order to make valid comparisons between different half-cells. So **standard conditions** are used in these measurements, defined as follows:

- all solutions must have a concentration of 1.0 mol dm^{-3};
- all gases must be at a pressure of 100 kPa;
- all substances used must be pure;
- temperature is 298 K;
- if the half-cell does not include a solid metal, platinum is used as the electrode.

Half-cells under these conditions are known as **standard half-cells**.

Figure 9.12 Fe^{2+}(aq)/Fe^{3+}(aq) half-cell. As it does not include a metal electrode, platinum is used as a point for the entry and exit of electrons into the half-cell. The platinum does not take part in the redox reaction. The standard hydrogen electrode uses platinum for the same purpose.

platinum electrode

solution containing Fe^{2+}(aq) and Fe^{3+}(aq) both at 1.0 mol dm^{-3}

When the standard hydrogen electrode is connected to another standard half-cell by an external circuit with a high-resistance voltmeter and a salt bridge, the EMF generated is known as the **standard electrode potential** of that half-cell. It is given the symbol $E^{\ominus}$. (E refers to electrode potential and the superscript $^{\ominus}$ refers to standard conditions, as introduced in Chapter 5.)

voltmeter

+0.34 V

e$^-$ e$^-$

salt bridge

H_2(g) at 298 K and 100 kPa

standard hydrogen electrode

anode

1.0 mol dm^{-3} H^+(aq)

cotton wool

Cu — cathode

Cu^{2+}

copper sulfate solution 1.0 mol dm^{-3}

$$H_2(g) \rightarrow 2H^+(aq) + 2e^- \qquad Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$
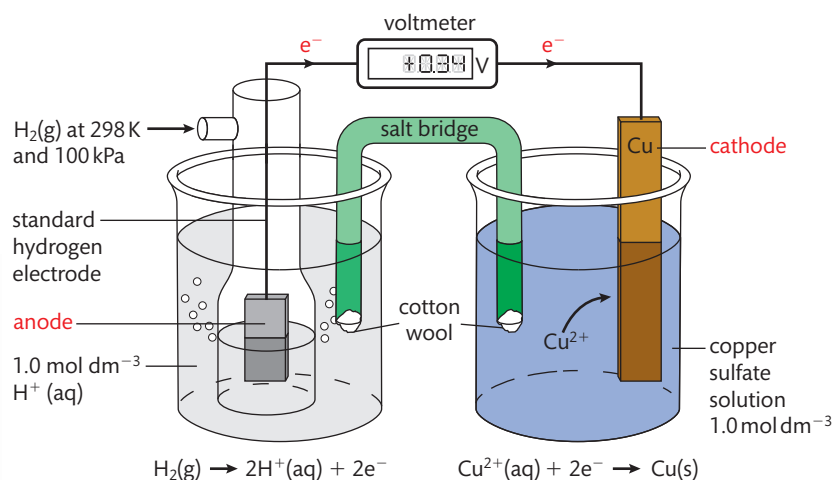
Figure 9.13 Measuring the standard electrode potential for Cu^{2+}(aq)/Cu(s).

For example, as shown in Figure 9.12, $E^{\ominus}$ for the Cu^{2+}(aq)/Cu(s) half-cell is +0.34 V.
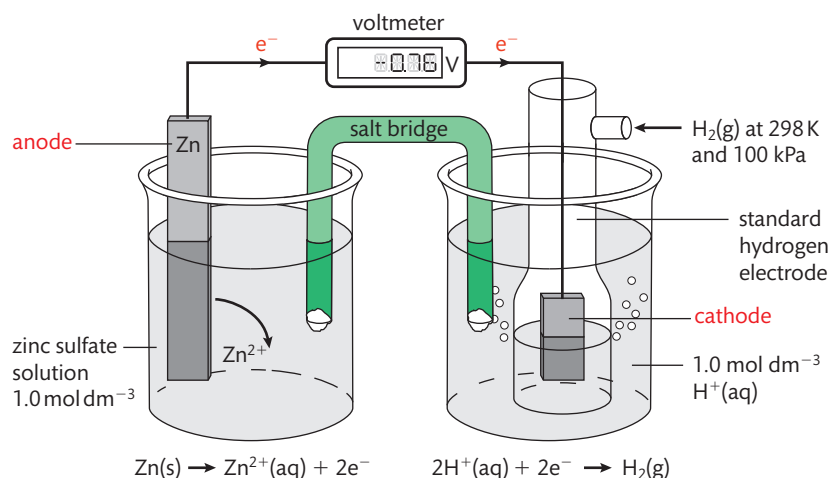
The positive value for $E^{\ominus}$ indicates that this half-cell has a greater tendency to be reduced than H^+. So electrons tend to flow from the hydrogen half-cell, which is therefore oxidized, to the copper half-cell, which is reduced.

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

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$
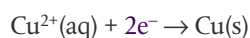
The hydrogen half-cell is the anode and the copper half-cell is the cathode, defined by the processes that occur there. The overall reaction is therefore:

$$Cu^{2+}(aq) + H_2(g) \rightarrow 2H^+(aq) + Cu(s) \qquad E^\ominus_{cell} = +0.34\ V$$

Copper is somewhat of an unusual metal in this respect, having a higher tendency to be reduced than H^+. More reactive metals lose their electrons very readily and so bring about the reduction of H^+. In these cases, the electron flow will be towards hydrogen and the $E^\ominus$ of the metal half-cell will be negative.

Figure 9.14 Measuring the standard electrode potential for $Zn^{2+}(aq)/Zn(s)$.

For example, as shown in Figure 9.14, $E^\ominus$ for the $Zn^{2+}(aq)/Zn(s)$ half-cell is –0.76 V.

The negative value for $E^\ominus$ indicates that this half-cell has less of a tendency to be reduced than H^+. So electrons flow from the zinc half-cell, which is therefore oxidized, to the hydrogen half-cell, which is reduced.

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

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$
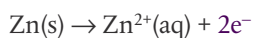
So the zinc half-cell is the anode and the hydrogen half-cell is the cathode. The overall reaction is therefore:

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \qquad E^\ominus_{cell} = -0.76\ V$$

These two examples also explain something we observed in Chapter 8. Most metals react with dilute acids, forming a salt with the liberation of hydrogen, but copper is unable to react in this way. We now see that this is because copper has a higher $E^\ominus$ than hydrogen, and so cannot reduce H^+. This is true for any metal that has a positive value for $E^\ominus$.

We can represent the zinc–hydrogen cell using the cell diagram convention we introduced earlier.
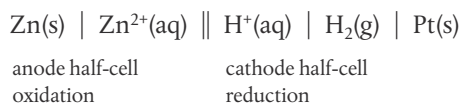
$$Zn(s)\ |\ Zn^{2+}(aq)\ \|\ H^+(aq)\ |\ H_2(g)\ |\ Pt(s)$$

anode half-cell   cathode half-cell
oxidation   reduction

Standard electrode potentials are given for the reduction reaction

Given that half-cell reactions exist as equilibria and can occur as oxidation or as reduction, for purposes of standardizing the data there has to be an agreed convention. The standard electrode potential is always given for the *reduction* reaction, in other words for the reaction with the oxidized species on the left and the reduced species on the right. For this reason, standard electrode potential values, $E^{\ominus}$, are sometimes known as **standard reduction potentials**.

A selection of standard electrode potential values is given in section 24 in the IB data booklet. Data from this table corresponding to half-cells discussed so far in this chapter are given here.

	Oxidized species		Reduced species	$E^{\ominus}$ / V, at 298 K
increasing tendency to occur as reduction	$Zn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Zn(s)$	−0.76
	$H^+(aq) + e^-$	$\rightleftharpoons$	$\frac{1}{2}H_2(g)$	0.00
	$Cu^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Cu(s)$	+0.34
	$Ag^+(aq) + e^-$	$\rightleftharpoons$	$Ag(s)$	+0.80

The following points should be noted:

- all $E^{\ominus}$ values refer to the reduction reaction;
- the $E^{\ominus}$ values do not depend on the total number of electrons, so do not have to be scaled up or down according to the stoichiometry of the equation;
- the more positive the $E^{\ominus}$ value for a half-cell, the more readily it is reduced.

It follows that electrons always flow through the external circuit in a voltaic cell from the half-cell with the more negative standard electrode potential to the half-cell with the more positive electrode potential. So the half-cell with the more negative electrode potential (–) is the anode as oxidation occurs there, and the half-cell with the more positive electrode potential (+) is the cathode as reduction occurs there.

> In a voltaic cell the half-cell with the higher (more positive) electrode potential is the cathode (+), and the half-cell with the lower (more negative) electrode potential is the anode (–).

> Electrons always flow towards the half-cell with the highest $E^{\ominus}$ value.

Using standard electrode potential data

Because the heights of mountains are all measured relative to sea level, we can deduce the difference in height between any two mountains and in which direction we would be going – uphill or downhill. In a similar way, the fact that standard electrode potential data are all referenced to the same point provides a relative scale for us to make predictions about redox reactions and the direction of electron flow. We will look at three specific applications of using $E^{\ominus}$ data here.

1 Calculating the cell potential, $E^{\ominus}_{cell}$

From the $E^{\ominus}$ values for any two half-cells, we can calculate the EMF for a voltaic cell in which they are connected. By deducing the direction of electron flow, we can also predict the outcome of a redox reaction.

The half-cell with the higher $E^{\ominus}$ value will be reduced, and the half-cell with the lower $E^{\ominus}$ value will be oxidized. As the cell potential is the difference in the tendencies of these two half-cells to be reduced, we can calculate it by substituting the appropriate values into the following expression:

$$E^{\ominus}_{cell} = E^{\ominus}_{\text{half-cell where reduction occurs}} - E^{\ominus}_{\text{half-cell where oxidation occurs}}$$
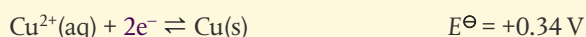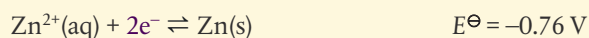
Note the following:

- The $E^{\ominus}$ values used in this expression must be the *reduction* potentials as supplied in data tables. Do not invert them before substituting into the equation!
- The $E^{\ominus}$ values do not have to be multiplied according to the stoichiometry of the redox equation. This is because they are intensive quantities and do not depend on the total number of electrons shown in the equation.

Worked example

Calculate the EMF for a voltaic cell constructed from a zinc half-cell and a copper half-cell, and identify the anode and cathode. Write the equation for the overall cell reaction.

Solution

Standard electrode potential data for these half-cells at 298 K are:

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad E^{\ominus} = -0.76 \text{ V}$$

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

So the copper half-cell will be reduced (higher value for $E^{\ominus}$), and the zinc half-cell will be oxidized. Electrons flow from zinc to copper.

$$E^{\ominus}_{cell} = E^{\ominus}_{\text{half-cell where reduction occurs}} - E^{\ominus}_{\text{half-cell where oxidation occurs}}$$

$$E^{\ominus}_{cell} = E^{\ominus}_{Cu^{2+}} - E^{\ominus}_{Zn^{2+}} = +0.34 - (-0.76) \text{ V} = +1.10 \text{ V}$$

The zinc half-cell is the anode and the copper half-cell is the cathode.
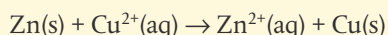
$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$
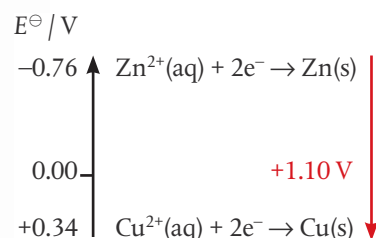
This confirms the value shown on the photograph on page 428.

$E^{\ominus}_{cell} = E^{\ominus}_{\text{half-cell where reduction occurs}} - E^{\ominus}_{\text{half-cell where oxidation occurs}}$

$E^{\ominus}$ / V

-0.76	$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$
0.00	$+1.10$ V
$+0.34$	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
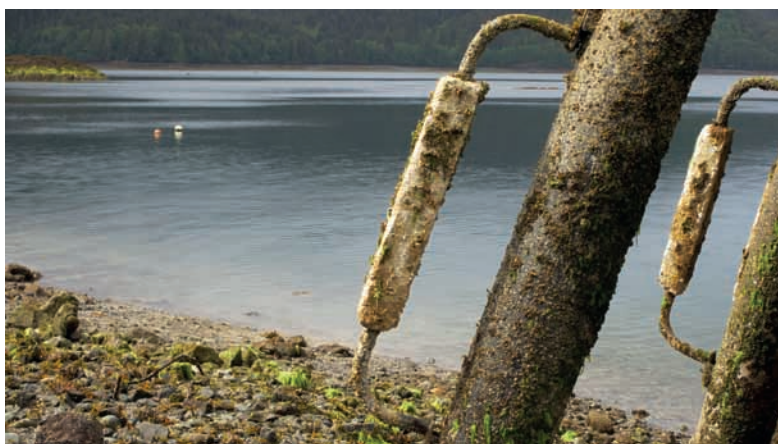
Cathodic protection. Blocks of zinc are bolted on to the iron posts to help protect the iron from corrosion. As zinc is preferentially oxidized, it acts as the anode where **sacrificial corrosion** occurs, $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$. This leaves the iron unaffected at the cathode. Photographed in Haida Gwaii, Canada.

Worked example

Determine $E^{\ominus}_{cell}$ for the voltaic cell based on the following two half-cells, for which $E^{\ominus}$ values are given. Write the equation for the overall reaction, and represent the cell with a cell diagram.

(i) $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$ $\qquad E^{\ominus} = +1.51 \text{ V}$

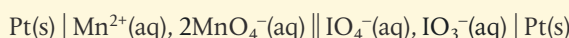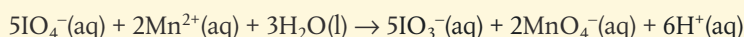(ii) $IO_4^-(aq) + 2H^+(aq) + 2e^- \rightleftharpoons IO_3^-(aq) + H_2O(l)$ $\qquad E^{\ominus} = +1.60 \text{ V}$

Solution

IO_4^-(aq) will be reduced, as it has the higher $E^\ominus$ value, and Mn^{2+}(aq) will be oxidized.

$$E^\ominus_{cell} = E^\ominus_{\text{half-cell where reduction occurs}} - E^\ominus_{\text{half-cell where oxidation occurs}}$$

$$= +1.60\text{ V} - (+1.51\text{ V})$$

$$= +0.09\text{ V}$$

To balance the equations for electrons, multiply (i) by 2 and (ii) by 5. Then add the two half-equations together, cancelling out terms on both sides.

$$5IO_4^-(aq) + 2Mn^{2+}(aq) + 3H_2O(l) \rightarrow 5IO_3^-(aq) + 2MnO_4^-(aq) + 6H^+(aq)$$

$$Pt(s)\,|\,Mn^{2+}(aq),\, 2MnO_4^-(aq)\,\|\,IO_4^-(aq),\, IO_3^-(aq)\,|\,Pt(s)$$

anode half-cell	cathode half-cell
oxidation	reduction

Note that Pt is used in both half-cells since it is stable in these conditions and they do not contain a metal to conduct.

2 Determining spontaneity of a reaction

As $E^\ominus$ values can be used to predict the redox change that will occur among a mixture of reactants, it follows we can use them to determine whether a particular reaction will occur spontaneously. This is based on the fact that *a voltaic cell will always run in the direction that gives a positive value for the $E^\ominus_{cell}$*.

- If $E^\ominus_{cell}$ is positive, the reaction is spontaneous as written.
- If $E^\ominus_{cell}$ is negative, the reaction is non-spontaneous, and the reverse reaction is spontaneous.

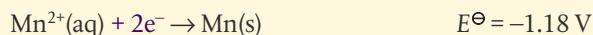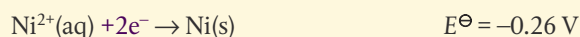$E^\ominus_{cell}$ **is positive for all spontaneous reactions.**

Worked example

Use $E^\ominus$ values to determine whether the reaction

$$Ni(s) + Mn^{2+}(aq) \rightarrow Ni^{2+}(aq) + Mn(s)$$
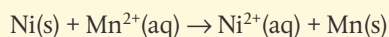
will occur spontaneously under standard conditions.

Solution

The data values are as follows:

$$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s) \qquad\qquad E^\ominus = -0.26\text{ V}$$

$$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s) \qquad\qquad E^\ominus = -1.18\text{ V}$$
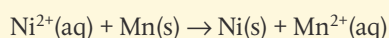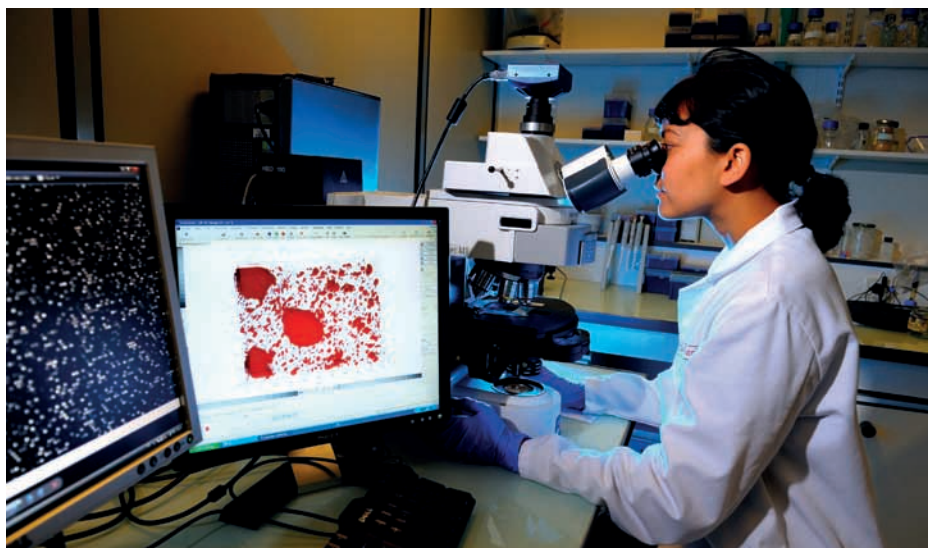
In the reaction given, Ni is being oxidized and Mn^{2+} is being reduced.

Substituting in the equation:

$$E^\ominus_{cell} = E^\ominus_{\text{half-cell where reduction occurs}} - E^\ominus_{\text{half-cell where oxidation occurs}}$$

$$E^\ominus_{cell} = E^\ominus_{Mn^{2+}} - E^\ominus_{Ni^{2+}} = -1.19 - (-0.26) = -0.93\text{ V}$$

The negative sign for $E^\ominus_{cell}$ tells us that this reaction will not happen spontaneously. In this mixture the reaction that occurs will be the reverse reaction,

$$Ni^{2+}(aq) + Mn(s) \rightarrow Ni(s) + Mn^{2+}(aq)$$

NATURE OF SCIENCE

Research into microbial fuel cells (MFCs) is a good example of the interdisciplinary nature of much scientific research. In this case, the combination of expertise in engineering and design technology with microbiology, molecular biology, and chemistry helps scientists understand how microbial ecosystems work and can be used to generate electricity. Teamwork and collaboration can create a synergy, in which the combined product of understanding is greater than the individual contributions. In research this can help to achieve a common goal that is beyond one scientific field.

Electrode potential and free energy change (E_{cell} and ΔG)

We have now come across two quantitative measures of the spontaneity of a reaction, $E_{\text{cell}}^{\ominus}$ and the free energy, $\Delta G^{\ominus}$, introduced in Chapter 5. These two values are directly related through the equation:

$$\Delta G^{\ominus} = -nFE^{\ominus}$$

where

- n = number of moles of electrons transferred in the reaction;
- F = the charge carried by 1 mole of electrons, known as the Faraday constant (it has a value of approximately 96 500 C mol^{-1}).

The units of the terms in this equation confirm the relationship:

$$\Delta G^{\ominus} \text{ (J)} = -n \text{ (mol) } F \text{ (C mol}^{-1}\text{) } E^{\ominus} \text{ (V) as J = C × V}$$

The negative sign in the equation indicates that E and ΔG have opposite signs:

- when $E_{\text{cell}}^{\ominus}$ is positive, $\Delta G^{\ominus}$ is negative $\Rightarrow$ reaction is spontaneous;
- when $E_{\text{cell}}^{\ominus}$ is negative, $\Delta G^{\ominus}$ is positive $\Rightarrow$ reaction is non-spontaneous;
- when $E_{\text{cell}}^{\ominus}$ is 0, $\Delta G^{\ominus}$ is 0 $\Rightarrow$ reaction is at equilibrium.

Because of the direct relationship between $E_{\text{cell}}^{\ominus}$ and $\Delta G^{\ominus}$, the more positive the value of $E_{\text{cell}}^{\ominus}$, the more energetically favourable is the reaction. It also follows that a voltmeter can be considered as an indirect measure of free-energy change as well as of electrode potential.

This equation enables us to calculate the free-energy change of a reaction from standard electrode potential data.

> **!** The equation $\Delta G^{\ominus} = -nFE^{\ominus}$ and the value of F are given in sections 1 and 2 of the IB data booklet.

CHALLENGE YOURSELF

5 Derive a more precise value of the Faraday constant using information in the IB data booklet.

CHALLENGE YOURSELF

6 In Chapter 7 we introduced an equation that relates the free-energy change of a reaction to its equilibrium constant. Here we have used an equation that relates the free-energy change to the electrode potential. Formulate an equation that combines these two equations, including a value for the combined constants at 298 K.

Worked example

Calculate the standard free-energy change at 298 K for the zinc–copper voltaic cell, which has a standard cell potential of +1.10 V.

Solution

First write the equation for the overall cell reaction, as we need to know the number of electrons transferred. We deduced this on page 437.

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

$$\Delta G^{\ominus} = -nFE^{\ominus}$$
$$= -2 \, (\text{mol e}^-) \times 96\,500 \, (\text{C mol}^{-1}) \times 1.10 \, (\text{V})$$
$$= 212{,}000 \, \text{J}$$
$$\therefore \Delta G^{\ominus} = -212 \, \text{kJ}$$

In practice, voltaic cells rarely run under standard conditions, and in any case the concentrations change as the reaction proceeds. A modification of the equation above, known as the **Nernst equation**, is used to calculate cell potentials under non-standard conditions. This is discussed in Option C, Energy.

3 Comparing relative oxidizing and reducing power of half-cells

The calculations using $E^{\ominus}$ values for half-reactions confirm the order of the activity series discussed earlier in this chapter. In quantitative terms, we can now say that a metal is able to reduce the ions of another metal that has a higher $E^{\ominus}$ value. Metals with low $E^{\ominus}$ values (most negative) are therefore the strongest reducing agents. Likewise, a non-metal is able to oxidize the ions of another non-metal that has a lower $E^{\ominus}$ value. Non-metals with high $E^{\ominus}$ values are therefore the strongest oxidizing agents.
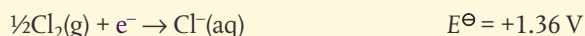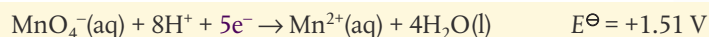
These trends are summarized below.

	Oxidized species		Reduced species	$E^{\ominus}$ / V	
increasing strength as oxidizing agent	$Zn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Zn(s)$	−0.76	increasing strength as reducing agent
	$H^+(aq) + e^-$	$\rightleftharpoons$	$\frac{1}{2}H_2(g)$	0.00	
	$Cu^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Cu(s)$	+0.34	
	$\frac{1}{2}I_2(s) + e^-$	$\rightleftharpoons$	$I^-(aq)$	+0.54	
	$\frac{1}{2}Cl_2(g) + e^-$	$\rightleftharpoons$	$Cl^-(aq)$	+1.36	

Worked example

A solution containing potassium manganate(VII) and concentrated hydrochloric acid reacts to form chlorine gas. Identify the strongest oxidizing agent in the solution and calculate the standard cell potential.

Solution

First consider the ions present in solution and extract the relevant half-equations from section 24 in the IB data booklet.

$$MnO_4^-(aq) + 8H^+ + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l) \qquad E^{\ominus} = +1.51 \text{ V}$$

$$\tfrac{1}{2}Cl_2(g) + e^- \rightarrow Cl^-(aq) \qquad E^{\ominus} = +1.36 \text{ V}$$

$MnO_4^-(aq)$ is the stronger oxidizing agent as it has the higher value for $E^{\ominus}$ so it will be reduced.

$$E^{\ominus}_{cell} = E^{\ominus}_{\text{half-cell where reduction occurs}} - E^{\ominus}_{\text{half-cell where oxidation occurs}}$$

$$E^{\ominus}_{cell} = E^{\ominus}_{MnO_4^-} - E^{\ominus}_{Cl_2} = +1.51 - (+1.36) = +0.15 \text{ V}$$

A little caution about interpreting $E^{\ominus}$ data

Note that although $E^{\ominus}$ data give information on the energetic feasibility of a reaction and the products of a redox reaction, they do not give any information on the rate. So a reaction that is predicted to be spontaneous may give no observable sign of reaction because the activation energy may be too high for the reaction to occur at an appreciable rate. As we saw in Chapters 6 and 7, feasibility and rate are two different considerations.

In addition, the $E^{\ominus}$ values that we have used throughout these examples relate only to standard conditions, and any changes in temperature, concentration, or pressure will alter the values, possibly even changing whether a reaction is spontaneous or not.
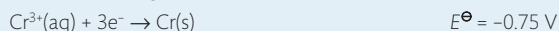
In summary, the interpretation of electrode potential data involves recognizing one fundamental fact: *electrons always tend to flow towards the half-cell with the highest $E^{\ominus}$ value*. All other deductions and interpretations follow from this.
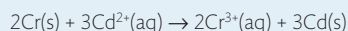
> **The higher the value of $E^{\ominus}$ of a half-cell, the stronger the oxidizing agent; the lower the value of $E^{\ominus}$, the stronger the reducing agent.**
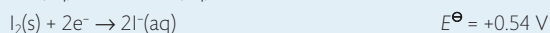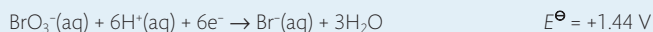
Exercises

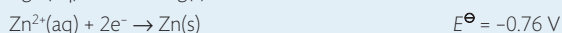**16** Given the standard electrode potentials of the following reactions:
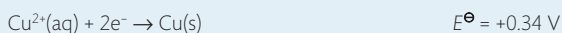
$$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s) \qquad E^{\ominus} = -0.75 \text{ V}$$
$$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s) \qquad E^{\ominus} = -0.40 \text{ V}$$

calculate the cell potential for

$$2Cr(s) + 3Cd^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Cd(s)$$

17 From the half-equations below, determine the cell reaction and standard cell potential.

$$BrO_3^-(aq) + 6H^+(aq) + 6e^- \rightarrow Br^-(aq) + 3H_2O \qquad E^{\ominus} = +1.44 \text{ V}$$
$$I_2(s) + 2e^- \rightarrow 2I^-(aq) \qquad E^{\ominus} = +0.54 \text{ V}$$

18 From the following data

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad E^{\ominus} = +0.34 \text{ V}$$
$$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s) \qquad E^{\ominus} = -2.37 \text{ V}$$
$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s) \qquad E^{\ominus} = -0.76 \text{ V}$$
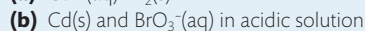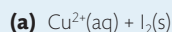
identify the strongest oxidizing agent and the strongest reducing agent.

19 Using the data for $E^{\ominus}$ values in questions 16–18, predict whether a reaction will be spontaneous between the following pairs.

(a) $Cu^{2+}(aq) + I_2(s)$
(b) $Cd(s)$ and $BrO_3^-(aq)$ in acidic solution
(c) $Cr(s)$ and $Mg^{2+}(aq)$
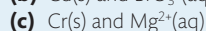
Write equations and calculate the cell potentials for the reactions that will occur as written.

20 The standard electrode potential for the reaction

$$Al(s) + Cr^{3+}(aq) \rightarrow Al^{3+}(aq) + Cr(s)$$
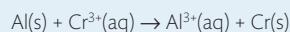
is 0.92 V at 298 K. What is the standard free-energy change for this reaction?

Electrolytic cells

An external source of electricity drives non-spontaneous redox reactions

Worker siphoning off molten aluminium in an aluminium processing plant. Electrolysis of a solution of alumina (Al_2O_3) dissolved in cryolite is used to reduce the Al^{3+} ions at the cathode. The molten aluminium is siphoned off and cooled before any further processing.

As we have seen, a voltaic cell takes the energy of a spontaneous redox reaction and harnesses it to generate electrical energy. An **electrolytic cell** does the reverse: it uses an external source of electrical energy to bring about a redox reaction that would otherwise be non-spontaneous. You can think of it in terms of an external power supply pumping electrons into the electrolytic cell, driving reactions of oxidation and reduction. As the word *electro-lysis* suggests, it is the process where electricity is used to bring about reactions of chemical breakdown.

The reactant in the process of electrolysis is present in the **electrolyte**. This is a liquid, usually a molten ionic compound or a solution of an ionic compound. As the electric current passes through the electrolyte, redox reactions occur at the **electrodes**, removing the charges on the ions and forming products that are electrically neutral. The ions are therefore said to be **discharged** during this process.

Reactive metals, including aluminium, lithium, magnesium, sodium, and potassium, are found naturally in compounds such as Al_2O_3 and NaCl where they exist as positive ions. Extraction of the metal therefore involves reduction of these ions. But this is a problem because, as we saw earlier, the $E^\ominus$ values of these reactive metal ions are so low that there are no good reducing agents available to do this.

In these cases, the only effective source of reduction is directly with electrons, using electrolysis. This means that electrolysis is the *only* means of extracting these metals from their ores. As we will see, it is also the process used in the production of many non-metal elements of industrial importance, and in the related procedures of electroplating and anodization.

The components of an electrolytic cell are shown in Figure 9.15 and described below.

Electrodes are electronically conducting, electrolytes are ionically conducting.
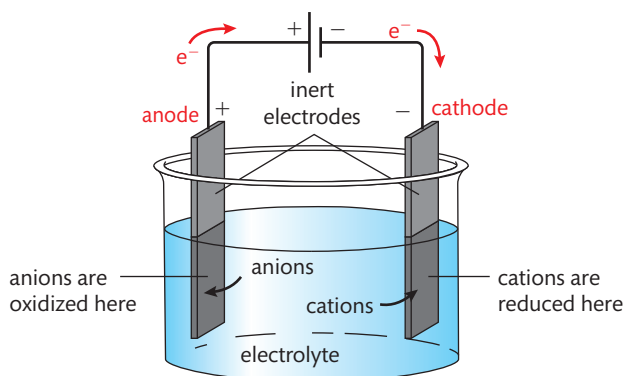
- The source of electric power is a battery or a DC power source. This is shown in diagrams as | | where the longer line represents the positive terminal and the shorter line the negative terminal.
- The electrodes are immersed in the electrolyte and connected to the power supply. They must not touch each other! Electrodes are made from a conducting substance – generally a metal or graphite. They are described as **inert** when they do not take part in the redox reactions.
- Electric wires connect the electrodes to the power supply.

The power source pushes electrons towards the negative electrode where they enter the electrolyte. This is the cathode. Electrons are released at the positive terminal, the anode, and returned to the source. The current is passed through the electrolyte, not by electrons but by the ions as they are mobile and migrate to the electrodes. The chemical reactions occurring at each electrode remove the ions from the solution and so enable the process to continue.

Redox reactions occur at the electrodes

The ions in the electrolyte migrate to the electrodes by attraction of opposite charges. So positive ions (cations) are attracted to the negative electrode, the cathode, while negative ions (anions) are attracted to the positive electrode, the anode. At the electrodes, redox reactions occur, oxidation at the anode and reduction at the cathode, which result in the ions being discharged. In aqueous solutions, water can be oxidized to oxygen at the anode and reduced to hydrogen at the cathode.

- At the negative electrode (cathode): $M^+ + e^- \rightarrow M$
  cations gain electrons so are reduced.
- At the positive electrode (anode): $A^- \rightarrow A + e^-$
  anions lose electrons so are oxidized.

Terminology of electrodes – a reminder

You will notice that the charges on the electrodes are inverted in an electrolytic cell compared with a voltaic cell. This is because it is the nature of the redox reaction, not the electrical charge, which defines the electrode: oxidation *always* occurs at the anode and reduction at the cathode, so electrons flow from anode to cathode. This never changes.

Michael Faraday, the English physicist and chemist (1791–1867), first defined and introduced the names electrolyte, electrode, anode, cathode, ion, anion, and cation, all of which are derived from Greek, into scientific language in 1834. He recognized the need to clarify the terminology, seeing the electrodes as surfaces where the current enters (anode) and leaves (cathode) the 'decomposing body' (electrolyte). He was referring to the established convention that current direction is always stated in reverse direction to electron flow. Faraday rather modestly suggested his names would be used only when necessary to avoid confusion, saying '*I am fully aware that names are one thing and science another*'.

At the anode negative ions lose electrons; at the cathode positive ions gain electrons.

	Voltaic cell		Electrolytic cell	
Anode	oxidation occurs here	negative	oxidation occurs here	positive
Cathode	reduction occurs here	positive	reduction occurs here	negative

Determining the products in electrolytic cells

We can apply our knowledge of redox chemistry to electrolytic cells, determining the reactions that occur at the electrodes, and so predicting the products released. The following steps are a useful summary.

1 Identify all the ions present in the electrolyte and determine which will migrate to which electrode: anions to anode, and cations to cathode.

2 Where there is more than one possible reaction at each electrode, determine which will occur, as will be discussed on page 447. Write the half-equation for the reaction at each electrode, showing electrons released at the anode in oxidation and taken up at the cathode in reduction.

3 Balance the electrons lost and gained at the anode and the cathode, then add the two half-equations to write the equation for the net reaction.

4 Consider what changes would be observed in the cell as a result of the redox processes occurring. These may include colour changes in the electrolyte, precipitation of solid, gas discharge, or pH changes.

## The electrolysis of molten salts

When the electrolyte is a molten salt, the only ions present are those from the compound itself as there is no solvent. So, usually, only one ion migrates to each electrode, and it is straightforward to predict the reactions that will occur.

Worked example

Describe the reactions that occur at the two electrodes during the electrolysis of molten lead(II) bromide. Write an equation for the overall reaction and comment on any likely changes that would be observed.
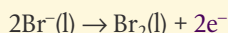
Solution

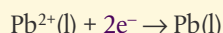**1** Deduce the ions present in the electrolyte and to which electrode they will be attracted:
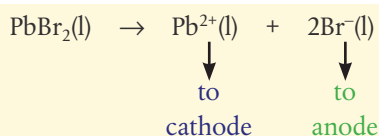
Lead(II) bromide has a relatively low melting point of 373 °C, so this electrolysis experiment can be carried out in a school laboratory. Unfortunately though, as the two products lead and bromine are both toxic, it may not be practical to do this.

Most other ionic compounds have very high melting points, so electrolysis of their molten salts involves working at high temperatures, which can only be generated and maintained under industrial conditions. Sometimes in industrial processes another compound is added to lower the melting point to make it more economical. For example, the electrolysis of molten sodium chloride used in the extraction of sodium uses an electrolyte of molten sodium chloride to which some molten calcium chloride has been added. This has a melting point of about 580 °C, considerably lower than the 801 °C for pure NaCl. It is obviously important though that the presence of the added $CaCl_2$ does not interfere with the discharge of sodium at the cathode. We can check that this is the case by looking at the $E^\ominus$ values for the two metal ions.

$$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s) \qquad E^\ominus = -2.87\ V$$

$$Na^+(aq) + e^- \rightarrow Na(s) \qquad E^\ominus = -2.71\ V$$

From its higher $E^\ominus$ value, we can deduce that Na^+ will be reduced in preference to Ca^{2+}, so the addition of $CaCl_2$ will not interfere with the production of Na at the cathode.

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

$$2Na^+(l) + 2e^- \rightarrow 2Na(l)$$

molten Na collects

molten NaCl electolyte

Figure 9.16 Electrolysis of molten sodium chloride. Chloride ions are oxidized at the anode and sodium ions are reduced at the cathode. The overall equation is $2NaCl(l) \rightarrow 2Na(l) + Cl_2(g)$.

Worked example

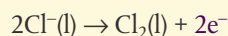Describe what you would expect to observe during the electrolysis of molten copper(II) chloride. Explain your answer in terms of the redox reactions occurring at the electrodes, including equations in your answer.
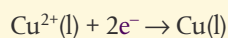
Solution

1
$$CuCl_2(l) \rightarrow Cu^{2+}(l) + 2Cl^-(l)$$

to cathode   to anode
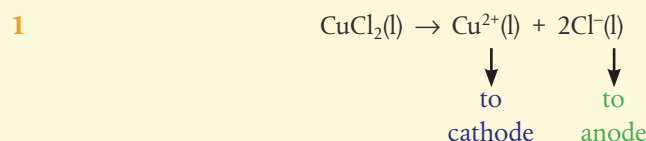
2   Half-equations at the electrodes are:

anode, Cl^- is oxidized:
$$2Cl^-(l) \rightarrow Cl_2(l) + 2e^-$$

cathode, Cu^{2+} is reduced:
$$Cu^{2+}(l) + 2e^- \rightarrow Cu(l)$$

3   Overall reaction: $Cu^{2+}(l) + 2Cl^-(l) \rightarrow Cu(l) + Cl_2(g)$

4   The observable changes will be a pale green gas with a pungent smell (Cl_2) around the anode, and a pinkish metallic solid (Cu) at the cathode. The bright blue colour of the solution will fade.

In the next section we will see how $E^\ominus$ data are used in similar ways to determine which ion is discharged when there is more than one anion or cation attracted to the same electrode.

Aluminium is a unique metal: strong, flexible, lightweight, corrosion-resistant, and 100% recyclable. Its commercial manufacture began in the 1880s when electrolysis made it possible to extract it from its ore bauxite, Al_2O_3. It is therefore a young metal in contrast to tin, lead, and iron, which have been in use for thousands of years, but in this short time it has become the world's second most used metal after steel. Aluminium production is, however, very energy intensive and also is associated with the production of perfluorocarbons (PFCs), strong greenhouse gases. A major emphasis must therefore be placed on recycling the metal as this uses only 5% of the energy and has only 5% of the greenhouse gas emissions compared with new production. Countries vary in the success of their recycling programmes; in the recycling of aluminium beverage cans Japan and Brazil are world leaders with rates over 95% cans recycled.

The aluminium drink can is the world's most recycled container, with approximately 70% of all cans being recycled worldwide.

21 Write half-equations for the electrode reactions occurring during the electrolysis of the following molten salts using graphite electrodes.

    (a) KBr   **(b)** MgF_2 **(c)** ZnS

22 Magnesium metal is produced by the electrolysis of molten magnesium chloride using inert electrodes.

    (a) Make a fully labelled drawing of the electrolytic cell, including the charges on the electrodes and the direction of electron and ion migration.

    (b) Write equations for the reactions occurring at each electrode and the overall cell reaction.

23 Which statement is *not* correct for the electrolysis of molten copper(II) chloride?

    A Copper ions and chloride ions move through the electrolyte.

    B Oxidation of chloride takes place at the anode.

    C Electrons move through the external circuit.

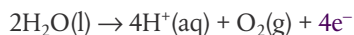   **D** Oxidation of chlorine takes place at the cathode.

Electrolysis of aqueous solutions

When electrolysis is carried out on an aqueous solution, predicting the products at the electrodes is more difficult because water itself can be oxidized or reduced.

• At the cathode, H_2O can be reduced to H_2:

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$
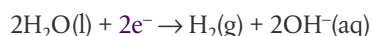
• At the anode, H_2O can be oxidized to O_2:

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

So when a solute M^+A^- is in an aqueous solution, there is more than one redox reaction possible at each electrode. Specifically:

• at the anode: either A^- or H_2O can be oxidized;

• at the cathode: either M^+ or H_2O can be reduced.

The discharge of an ion at the electrode in these cases is known as **selective discharge**. The outcome is determined by the following factors:

• **the relative $E^{\ominus}$ values of the ions;**

• **the relative concentrations of the ions in the electrolyte;**

• **the nature of the electrode.**

These are discussed below with reference to specific examples, using the steps given earlier.
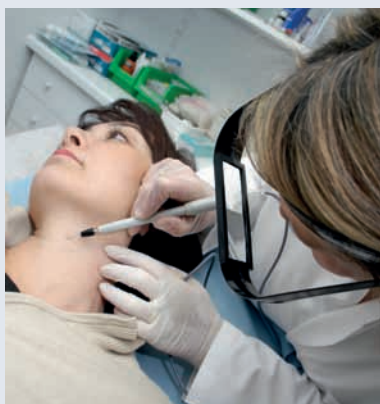
Electrolysis is used to remove unwanted hairs permanently. The needle is inserted into the hair shaft and passes an electric current through the follicle. Electrolytic reactions result in the production of NaOH, which destroys the hair follicle.

Electrolysis of water

As we learned in Chapter 8, the ionization of pure water is extremely low, so it is not a good conductor of electricity. However, the addition of ions increases its conductivity, so usually some ionic compound such as NaOH (which as we will see will not interfere with the discharge of the ions from water) is added when this electrolysis is performed.

1 Ions present:

$$NaOH(aq) \quad \rightarrow \quad Na^+(aq) \quad + \quad OH^-(aq)$$

to cathode   to anode

2 At the cathode, possible reactions are:

$$Na^+(aq) + e^- \rightarrow Na(s) \qquad\qquad E^\ominus = -2.71 \text{ V}$$

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad E^\ominus = -0.83 \text{ V}$$

So H_2O is preferentially reduced and $H_2(g)$ will be discharged.

At the anode, possible reactions are:

$$4OH^-(aq) \rightarrow 2H_2O(l) + O_2(g) + 4e^- \qquad -E^\ominus = -0.40 \text{ V}$$

$$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^- \qquad -E^\ominus = -1.23 \text{ V}$$
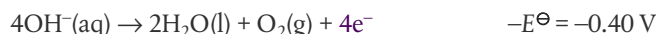
Note because these reactions are written as oxidations, the sign of the electrode potential has been reversed. Based on these values, $OH^-(aq)$ is preferentially oxidized and $O_2(g)$ is discharged.

3 The overall balanced equation is:

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

4 The observed changes at the electrodes will be:
- colourless gas evolved at both anode (O_2) and cathode (H_2)
- ratio by volumes of the gases is 2 H_2 : 1 O_2 (by application of Avogadro's law on gas volumes)
- the pH at the anode will decrease as H^+ is released, while the pH at the cathode will increase as OH^- is released.

This reaction, sometimes known as the 'splitting of water' is of great interest because of the demand for a cheap source of hydrogen to drive the so-called **hydrogen economy**. This refers to its use as an energy carrier, and its potential to replace fossil fuels, for example in cars and airplanes. There is considerable controversy though over the usefulness of a hydrogen economy, principally because of the energy demands of its production through electrolysis. Much research is focused on 'artificial photosynthesis' that attempts to replicate the process of water splitting that occurs in sunlight in green plants. A discovery that titanium compounds can act as photo-catalysts in the reaction of splitting water has stimulated interest in the possibility of producing hydrogen using solar rather than electrical energy, known as photo-electrosynthesis.
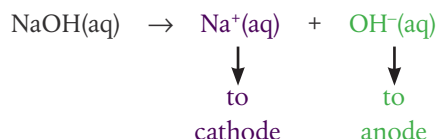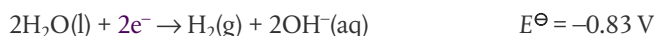
Apparatus to demonstrate the electrolysis of water. The battery on the left is the source of electrical energy that drives the reactions at the electrodes. Hydrogen is produced by reduction of H_2O at the cathode (on the right) and oxygen is produced by the oxidation of H_2O at the anode (on the left). The ratio of volumes of hydrogen : oxygen is 2 : 1 as shown by the stoichiometry of the equations.

Electrolysis of NaCl(aq)

NaCl(aq) is sometimes known as **brine**. Electrolysis of this solution leads to the production of $H_2(g)$, $Cl_2(g)$, and NaOH(aq), all of which are of commercial importance.

1 Ions present:

$$NaCl(aq) \quad \rightarrow \quad Na^+(aq) \quad + \quad Cl^-(aq)$$

$$\downarrow \qquad\qquad \downarrow$$

to to
cathode anode
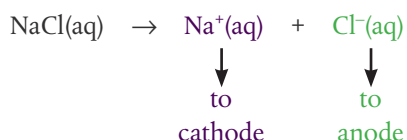
2 At the cathode the possible reactions are the same as above in the electrolysis of water. So H_2O is preferentially reduced and $H_2(g)$ will be discharged.

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

At the anode, possible reactions are:

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

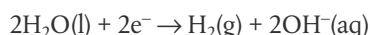$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^- \qquad\qquad -E^{\ominus} = -1.36 \text{ V}$$

Although the $E^{\ominus}$ value favours the oxidation of H_2O leading to the discharge of O_2, the situation here is a bit more complicated.

- When the concentration of Cl^- is low, H_2O is oxidized, leading to the release of O_2 as given in the electrolysis of water.
- But when, more typically, the concentration of NaCl is greater than about 25% by mass of the solution, the Cl^- is preferentially oxidized, leading to the release of $Cl_2(g)$. The industrial electrolysis of brine uses a saturated solution of aqueous NaCl to ensure the discharge of $Cl_2(g)$.

3 The overall balanced equation when Cl^- is discharged is:

$$2NaCl(aq) + 2H_2O(l) \rightarrow H_2(g) + Cl_2(g) + 2Na^+(aq) + 2OH^-(aq)$$
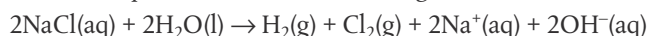
4 The observed changes at the electrodes (assuming Cl^- discharged) will be:
- gas evolved at both anode (Cl_2) and cathode (H_2);
- $Cl_2(g)$ identified at the anode through strong smell and bleaching effect on damp blue litmus paper;
- an increase in pH of the electrolyte will occur due to release of OH^-.

When a question asks you to describe the electrolysis of NaCl, be clear on whether it is about NaCl(l) or NaCl(aq). As you have seen here, they are different processes leading to distinct products and applications.

The commercial electrolysis of aqueous sodium chloride, known as the **chlor-alkali** industry, has been in operation since 1892. It is of major significance economically because of the simultaneous yield of Cl_2 and NaOH. One process, the mercury cell, produces chlorine-free NaOH, but is associated with serious health and environmental concerns because of the use of mercury, a known toxin. In 2013 the United Nations Environment Programme agreed to a deadline for the phase-out of mercury cells by 2025, and this was accepted by more than 140 countries.

The explanation given here about the preferential discharge of Cl^- when its concentration is high is valid, but somewhat of a simplification. A fuller interpretation includes the fact that $E^{\ominus}$ values reflect equilibrium conditions, but as ion distributions change while the current flows these potentials also change. In effect a higher voltage, known as **overvoltage**, must be applied to discharge an ion in an operating cell. In the electrolysis of NaCl(aq) where the pH increases during the reaction, there is a significant increase in the overvoltage for the oxidation of water, thus favouring the discharge of Cl^- at the anode. Electrode kinetics is also a factor; modern chlor-alkali anodes are titanium metal coated with a few microns of Ir and Ru oxides that catalyse the preferential oxidation of Cl^- to Cl_2.

Electrolysis of CuSO$_4$(aq)

CuSO$_4$(aq) is a bright blue colour, due to the presence of the hydrated Cu^{2+} ion. Electrolysis of this solution yields different products depending on the nature of the electrodes. We will describe the reactions with (a) C electrodes and (b) Cu electrodes here, following the same steps according to the numbered sequence on page 444.

The electrolytic processes involving copper are respectively called 'electro-winning' (C anode) and 'electro-refining' (Cu anode). In industry the electro-winning anode is usually a lead/antimony alloy.
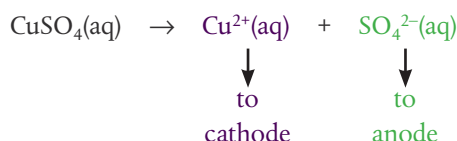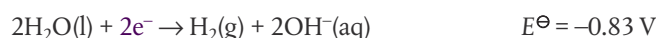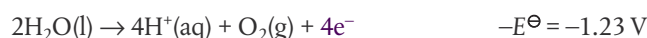
1 Ions present:

$$CuSO_4(aq) \rightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$$

$$\downarrow \qquad\qquad \downarrow$$

to cathode   to anode

(a) Carbon (graphite) or other 'inert' electrodes

2 At the cathode, possible reactions are:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad\qquad E^\ominus = +0.34 \text{ V}$$
$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \qquad\qquad E^\ominus = -0.83 \text{ V}$$

So Cu^{2+} is preferentially reduced and Cu(s) is discharged.

At the anode, H$_2$O is preferentially oxidized:

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

Selective discharge of an ion during electrolysis depends on relative $E^\ominus$ values, the ion concentration, and the nature of the electrode.

3 The overall balanced equation is:

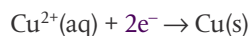$$2CuSO_4(aq) + 2H_2O(l) \rightarrow 2Cu(s) + O_2(g) + 4H^+(aq) + 2SO_4^{2-}(aq)$$
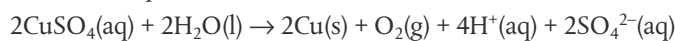
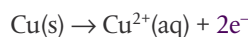**4** The observed changes at the electrodes are as follows:
- pinky brown colour of copper deposited on cathode;
- colourless gas (O$_2$) evolved at the anode;
- decrease in pH of the solution due to release of H$^+$ ions;
- loss of intensity of blue colour due to discharge of Cu^{2+}(aq).

(b) Copper electrodes

2 At the cathode: the reaction will be as above with discharge of Cu^{2+}:

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

At the anode: the reaction is different from above. The Cu electrode itself is oxidized, supplying electrons for the reaction and dissolving as Cu^{2+}(aq):

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

3 So the net reaction is the movement of Cu^{2+}(aq) from where it is produced at the anode to the cathode where it is discharged as Cu(s).

4 The observed changes at the electrodes are as follows:
- pinky brown colour of Cu deposited on cathode;
- disintegration of Cu anode;
- no change in the pH of the solution;
- no change in the intensity of the blue colour of the solution as Cu^{2+} ions are both formed and removed from the solution so their concentration remains constant.

An application of this is used in the purification of copper. The process uses electrolysis of a solution containing Cu^{2+}(aq) with an impure copper anode and a small pure copper cathode. As the cell runs, the anode erodes as copper is transferred to the

cathode, which therefore increases in mass. Impurities collect as sludge in the bottom of the cell.
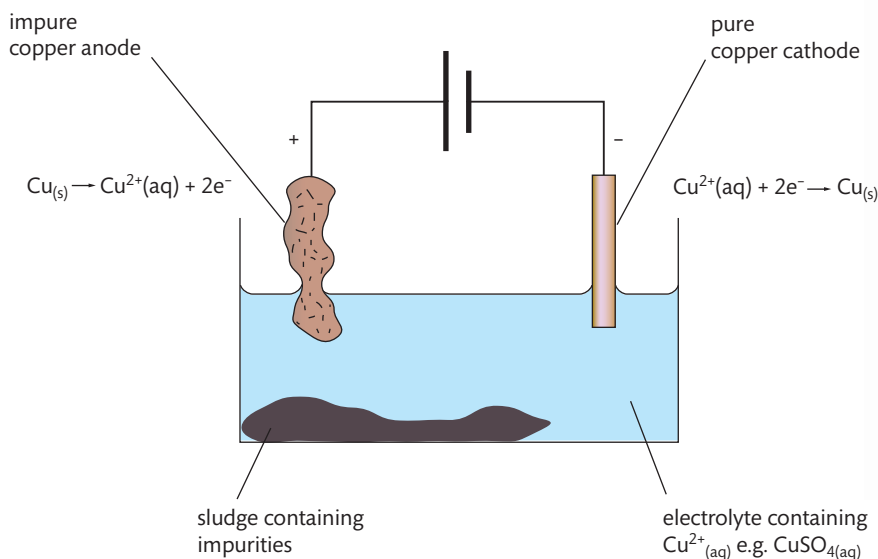

Figure 9.17 The purification of copper using electrolysis. Reactions at the electrodes result in a net transfer of copper from the anode to the cathode.

impure copper anode

pure copper cathode

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

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

sludge containing impurities

electrolyte containing $Cu^{2+}_{(aq)}$ e.g. $CuSO_{4(aq)}$

A close-up photograph of the coil-shape electrodes used in electrolysis of aqueous tin(II) chloride, $SnCl_2(aq)$. Deduce which electrode is which and write electrode reactions for the changes shown. What can you deduce about the electrode potential of Sn^{2+}?

Exercises

24 Deduce the products formed during the electrolysis of an aqueous solution of potassium fluoride. Write an equation for the reaction at the anode and explain your reasoning.

25 (a) Describe fully all the changes you would expect to see during the electrolysis of $CuCl_2(aq)$ using carbon electrodes. Write equations to support your predicted observations.
   (b) How would your answer to (a) change if Cu electrodes were used instead?

26 Write an equation for a reaction that occurs during the electrolysis of NaCl(aq) that does not occur during the electrolysis of NaCl(l).

Factors affecting the amount of product in electrolysis

Michael Faraday, who, as noted earlier, coined the terminology used in much of this work, also showed that the amounts of products at the electrodes depend on the quantity of electric charge passed through the cell.
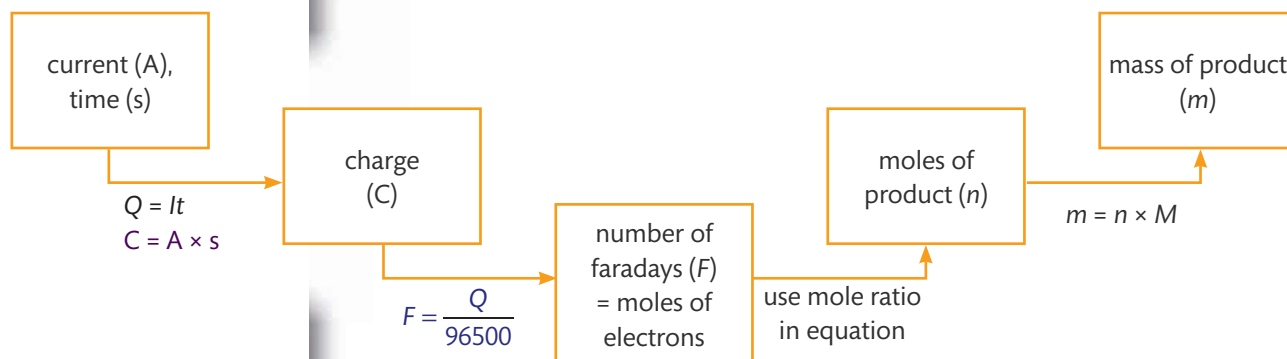

Historical artwork of Michael Faraday's experiments on electrolysis in 1833. By passing electricity through molten tin chloride he was able to show that the amounts of tin produced at the cathode and chlorine gas produced at the anode were proportional to the amount of electricity.
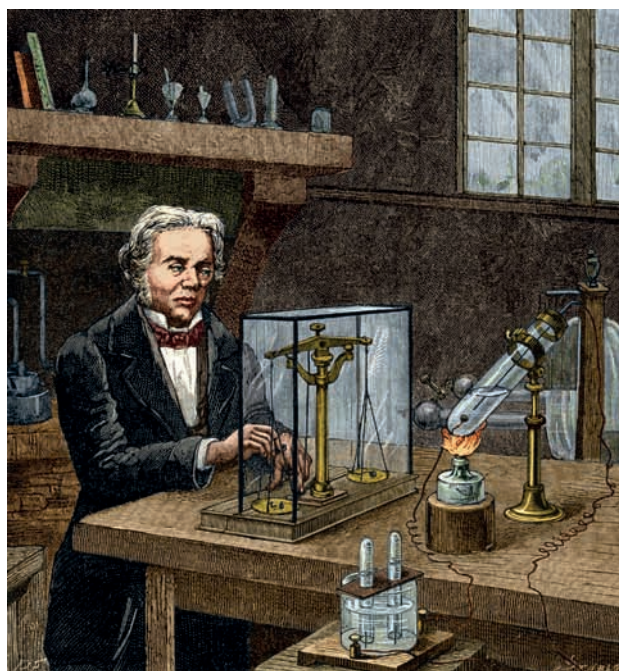
We can quantify electric charge as follows:

- charge = current × time

  So: Charge, Q measured in coulomb (C), depends on the current, I measured in amperes (A) and the time, t measured in seconds (s).

- The charge carried by one mole of electrons, known as a Faraday (F) introduced on page 432, is 96 500 C.

We can now relate laboratory measurements to the amounts of product as follows.

current (A), time (s) →
$$Q = It$$
$$C = A \times s$$
→ charge (C) →
$$F = \frac{Q}{96500}$$
→ number of faradays (F) = moles of electrons → use mole ratio in equation → moles of product (n) →
$$m = n \times M$$
→ mass of product (m)

Worked example

(a) How many grams of copper are deposited on the cathode of an electrolytic cell containing $CuCl_2$(aq) if a current of 2.00 A is run for 15.0 minutes?

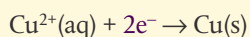**(b)** How would the amount differ if the same conditions were applied using CuCl(aq) instead?

Solution

(a) We first calculate the charge then the moles of electrons:

$$\text{charge} = \text{current} \times \text{time}$$
$$= 2.00 \text{ A} \times (15.0 \times 60 \text{ s})$$
$$= 1800 \text{ C}$$

$$F = \frac{1800 \text{ C}}{96500 \text{ C mol}^{-1}} = 0.01865 \text{ mol of e}^-$$

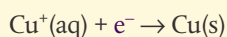Then use the mole ratio in the electrode half-equation to determine the moles of product:

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

$\Rightarrow$ 2 mol e$^-$: 1 mol Cu

$$\therefore 0.01865 \text{ mol e}^- \rightarrow \frac{0.01865 \text{ mol e}^-}{2 \text{ mol e}^-} \times 1 \text{ mol Cu} = 0.00933 \text{ mol Cu}$$

$$m = n \times M$$
$$= 0.00933 \text{ mol} \times 63.55 \text{ g mol}^{-1}$$
$$= 0.593 \text{ g Cu}$$
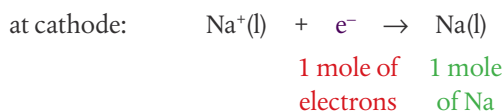
(b) The equation for discharge from CuCl(aq) is

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

$\Rightarrow$ 1 mol e$^-$: 1 mol Cu

$$\therefore 0.01865 \text{ mol e}^- \rightarrow 0.01865 \text{ mol Cu}$$

$$m = n \times M$$

$$\therefore 0.01865 \text{ mol e}^- \times 63.55 \text{ g mol}^{-1} = 1.19 \text{ g Cu}$$

We see that the same quantity of electric charge produces twice as much copper from Cu^+ as from Cu^{2+}. This shows that the charge on the ion also influences the amount of product and enables us to determine relative amounts. For example, in the electrolysis of NaCl(l) and PbBr$_2$(l) discussed earlier we can deduce:

NaCl(l) electrolyte

at cathode: $\quad$ Na$^+$(l) $\quad + \quad$ e$^- \quad \rightarrow \quad$ Na(l)

$\qquad\qquad\qquad\qquad$ 1 mole of $\quad$ 1 mole
$\qquad\qquad\qquad\qquad$ electrons $\qquad$ of Na

PbBr$_2$(l) electrolyte

at cathode: $\quad$ Pb^{2+}(l) $\quad + \quad$ 2e$^- \quad \rightarrow \quad$ Pb(s)

$\qquad\qquad\qquad\qquad$ 2 moles of $\quad$ 1 mole
$\qquad\qquad\qquad\qquad$ electrons $\qquad$ of Pb
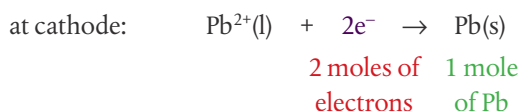
So to produce 1 mole of Pb requires twice the quantity of electricity required to produce 1 mole of Na.

> The amount of product formed in electrolysis is determined by the current, duration, and the charge on the ion.

Worked example

If a current of 2.00 A is passed through a solution of $AgNO_3$ for 10 minutes it is found that 0.0124 moles of Ag are formed.

(a) How much would form if a current of 1.00 A is passed through the same solution for 30 minutes?

(b) What amount of Cu would form if the quantity of electricity in (a) was passed through a solution of $CuSO_4$?

Solution

(a) charge = current × time

amount of product = $0.0124 \text{ mol} \times \dfrac{1.00 \text{ A}}{2.00 \text{ A}} \times \dfrac{30 \text{ min}}{10 \text{ min}}$ = 0.0186 mol Ag

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

So the same quantity of electricity will produce 2 Ag : 1 Cu

therefore yield Cu = $\dfrac{0.0186 \text{ mol}}{2}$ = 0.0093 mol Cu

In summary, we can conclude that the amount of products formed in electrolysis are determined by:

1 the current;
2 the duration of the electrolysis;
3 the charge on the ion.

Electroplating: a widely used application of electrolysis

During the electrolysis of $CuSO_4(aq)$, we saw that Cu(s) is deposited on the cathode when either graphite or copper electrodes are used. This is one example of **electroplating**, the process of using electrolysis to deposit a layer of a metal on top of another metal or other conductive object. An electrolytic cell used for electroplating has the following features:

• an electrolyte containing the metal ions which are to be deposited;
• the cathode made of the object to be plated;
• sometimes the anode is made of the same metal which is to be coated because it may be oxidized to replenish the supply of ions in the electrolyte.
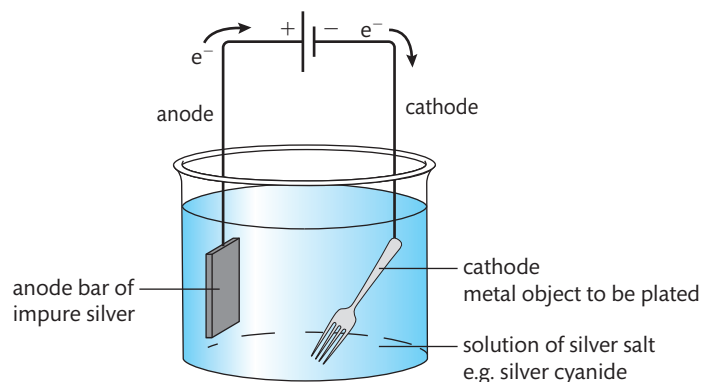
Techniques for electroplating plastics have developed over the last 50 years or so, and P–O–P (plated on plastic) components are now commonplace. These products have the appearance of a high quality metal with the advantage of significant weight reduction. This is particularly important in the automobile industry, and used for example in chromium-plated car trim. But as plastics are not conductors, they must first be treated in an aggressive chromic/sulfuric acid bath to make small pits on their surface. They are then placed in a palladium chloride bath to deposit metal particles in the pits, after which the plastics can be electroplated with chromium or other metals.

Figure 9.18 Apparatus for electroplating silver.

Reduction of the metal ions at the cathode leads to their deposition on its surface. The process can be controlled by altering the current and the time according to how thick a layer of metal is desired.

Electroplating serves many different purposes, some of which are outlined here.

- Decorative purposes. For example, covering a metal with a layer of a more expensive or decorative metal, such as silver- and nickel-plating of cutlery.
- Corrosion control. For example, iron with a layer of zinc deposited on its surface, known as **galvanized iron**, is protected from corrosion as the zinc will be preferentially oxidized. This is sometimes called **sacrificial protection**.
- Improvement of function. For example electroplating with chromium improves the wear on steel parts such as crankshafts and hand tools.

Metal-coated beetles. The metal has been added by electroplating.

Anodizing is an electrolytic process in which a metal anode is oxidized to deposit a metal oxide coat on the surface of the metal. This surface coat protects the underlying metal from corrosion. It is commonly applied to aluminium and chromium, and enables these metals to be used much more extensively than would be possible with the uncoated metal. For example, anodized aluminium is commonly used in cooking utensils and does not react even when heated despite its relatively high position in the reactivity series.

Summary of voltaic and electrolytic cells

We have seen that voltaic and electrolytic cells are the reverse of each other. A voltaic cell converts chemical energy to electrical energy when a reaction with a positive value for E proceeds towards equilibrium; an electrolytic cell converts electrical energy to chemical energy when an electric current drives a reaction with a negative value for E away from equilibrium. These relationships, together with the free-energy change ΔG, for the different cells are summarized below.

The Guggenheim museum, Bilbao, Spain, which opened in 1997, is sheathed in panels of titanium. Although the metal is very resistant to corrosion, when it is anodized using electrolysis, the layer of titanium oxide deposited on its surface changes its optical properties, causing it to have different colours in different lights.

Type of cell	E_{cell}	ΔG	Type of reaction
voltaic	> 0	< 0	spontaneous
electrolytic	< 0	> 0	non-spontaneous
equilibrium	0	0	dead battery

Exercises

27 If a quantity of electricity is passed through a molten sample of aluminium chloride, it is found that 0.2 moles of chlorine are formed. What is the mass of aluminium formed at the other electrode?

28 Which of the following will cause the largest amount of copper to be deposited during electrolysis?

    A   Cu(I)Cl(aq), 5.00 A, 10 min   **C**   Cu(I)Cl(aq), 2.00 A, 30 min
    B $Cu(II)Cl_2$, 5.00 A, 10 min   **D** $Cu(II)Cl_2$, 2.00 A, 30 min

29 A metal spoon is plated with silver using an aqueous solution of $AgNO_3$ and an impure silver anode. Predict how the masses of the two electrodes will change with time and what other changes might be visible.

Practice questions

1 Four electrolytic cells are constructed. Which cell would produce the greatest mass of metal at the negative electrode (cathode)?

	Electrolyte	Current / A	Time / s
A	1.0 mol dm^{-3} $CuSO_4$(aq)	1.0	500
B	1.0 mol dm^{-3} $AgNO_3$(aq)	2.0	250
C	1.0 mol dm^{-3} $CuSO_4$(aq)	1.0	750
D	1.0 mol dm^{-3} $AgNO_3$(aq)	1.5	250

2 Which species could be reduced to form NO_2?

    A N_2O **B** NO_3^- **C** HNO_2 **D** NO

3 The standard electrode potentials for two metals are given below.

$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$ $E^\ominus = -1.66$ V
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $E^\ominus = -0.23$ V

What is the equation and cell potential for the spontaneous reaction that occurs?

    A $2Al^{3+}(aq) + 3Ni(s) \rightarrow 2Al(s) + 3Ni^{2+}(aq)$ $E^\ominus = -1.89$ V
    B $2Al(s) + 3Ni^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Ni(s)$ $E^\ominus = -1.89$ V
    C $2Al^{3+}(aq) + 3Ni(s) \rightarrow 2Al(s) + 3Ni^{2+}(aq)$ $E^\ominus = -1.43$ V
    D $2Al(s) + 3Ni^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Ni(s)$ $E^\ominus = -1.43$ V

4 For the electrolysis of aqueous copper(II) sulfate, which of the following statements is correct?

    A   Cu and O_2 are produced in a mol ratio of 1 : 1
    B H_2 and O_2 are produced in a mol ratio of 1 : 1
    C   Cu and O_2 are produced in a mol ratio of 2 : 1
    D H_2 and O_2 are produced in a mol ratio of 2 : 1

5 Consider the following reaction.

$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$

Which statement is correct?

    A MnO_4^- is the oxidizing agent and it loses electrons.
    B MnO_4^- is the reducing agent and it loses electrons.
    C MnO_4^- is the oxidizing agent and it gains electrons.
    D MnO_4^- is the reducing agent and it gains electrons.

6 What condition is necessary for the electroplating of silver, Ag, onto a steel spoon?

    A The spoon must be the positive electrode.
    B The silver electrode must be the negative electrode.
    C The spoon must be the negative electrode.
    D The electrolyte must be acidified.

7 What is the reducing agent in the reaction below?

$$2MnO_4^-(aq) + Br^-(aq) + H_2O(l) \rightarrow 2MnO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$$
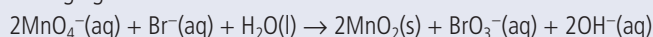
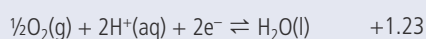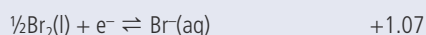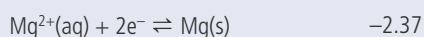   **A** Br^- **B** BrO_3^- **C** MnO_4^- **D** MnO_2

8 Which changes could take place at the positive electrode (cathode) in the voltaic cell?

    I $Zn^{2+}(aq)$ to $Zn(s)$
    II $Cl_2(g)$ to $Cl^-(aq)$
    III $Mg(s)$ to $Mg^{2+}(aq)$

    A I and II only   **B** I and III only   **C** II and III only   **D** I, II, and III

9 How do the products compare at each electrode when aqueous 1 mol dm^{-3} magnesium bromide and molten magnesium bromide are electrolysed?

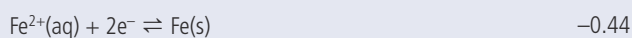 $E^{\ominus}$ / V

    $Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ −2.37

    $\frac{1}{2}Br_2(l) + e^- \rightleftharpoons Br^-(aq)$ +1.07

    $\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O(l)$ +1.23

	Positive electrode (anode)	Negative electrode (cathode)
A	same	same
B	same	different
C	different	same
D	different	different

10 What happens at the negative electrode in a voltaic cell and in an electrolytic cell?

	Voltaic cell	Electrolytic cell
A	oxidation	reduction
B	reduction	oxidation
C	oxidation	oxidation
D	reduction	reduction

**11** What is the cell potential, in V, for the reaction that occurs when the following two half-cells are connected?

                                                      $E^{\ominus}$ / V

    $Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$ −0.44

    $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$ +1.33

    A +0.01   **B** +0.89   **C** +1.77   **D** +2.65

12 (a) An electrochemical cell is made from an iron half-cell connected to a cobalt half-cell:
The standard electrode potential for $Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$ is –0.45 V. The total cell potential obtained when the cell is operating under standard conditions is 0.17 V. Cobalt is produced during the spontaneous reaction.
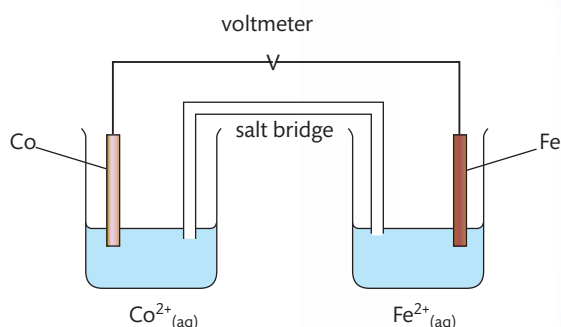

(i) Define the term *standard electrode potential* and state the meaning of the minus sign in the value of –0.45 V. (3)

(ii) Calculate the value for the standard electrode potential for the cobalt half-cell. (1)

(iii) Deduce which species acts as the oxidizing agent when the cell is operating. (1)

(iv) Deduce the equation for the spontaneous reaction taking place when the iron half-cell is connected instead to an aluminium half-cell. (2)

(v) Explain the function of the salt bridge in the electrochemical cell. (2)

(b) Deduce the oxidation number of cobalt in the following species.

(i) $[Co(H_2O)_6]^{2+}$ (1)

(ii) $Co_2(SO_4)_3$ (1)

(iii) $[CoCl_4]^{2-}$ (1)

(c) An electrolytic cell is made using a very dilute solution of sodium chloride.

(i) Draw a labelled diagram of the cell. Use an arrow to show the direction of the electron flow and identify the positive and negative electrodes. (3)

(ii) Give all the formulas of all the ions present in the solution. (2)

(iii) Predict the products obtained at each electrode and state the half-equation for the formation of each product. (3)

(iv) Deduce the molar ratios of the products obtained at the two electrodes. (1)

(d) Predict the products by giving the relevant half-equation for the reaction occurring at each electrode if the electrolyte of the cell described in part (c) was changed to:

(i) concentrated sodium chloride (2)

(ii) molten sodium bromide (2)

(*Total 25 marks*)

13 (a) Outline two differences between an electrolytic cell and a voltaic cell. (2)

(b) Explain why solid sodium chloride does not conduct electricity but molten sodium chloride does. (2)

(c) Molten sodium chloride undergoes electrolysis in an electrolytic cell. For each electrode deduce the half-equation and state whether oxidation or reduction takes place. Deduce the equation of the overall cell reaction including state symbols. (5)

(d) Electrolysis has made it possible to obtain reactive metals such as aluminium from their ores, which has resulted in significant developments in engineering and technology. State one reason why aluminium is preferred to iron in many uses. (1)

(e) Electroplating is an important application of electrolysis. State the composition of the electrodes and the electrolyte used in the silver electroplating process. (3)

(*Total 13 marks*)

14 Consider the following half-cell reactions and their standard electrode potentials.

$$E^{\ominus} / \text{V}$$

$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ -0.26

$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$ -1.66
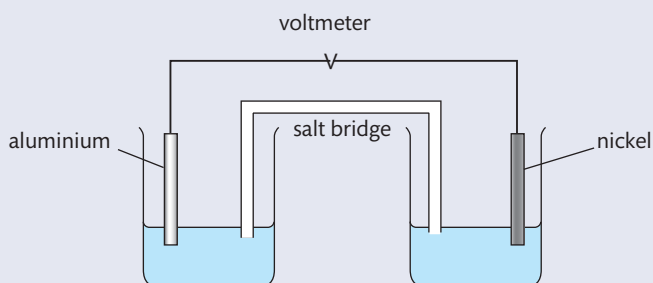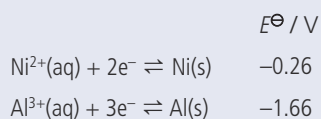
(a) Deduce a balanced equation for the overall reaction which will occur spontaneously when these two half-cells are connected. (2)

(b) Determine the cell potential when the two half-cells are connected. (1)

(c) On the cell diagram below, label the negative electrode (anode), the positive electrode (cathode), and the directions of the movement of electrons and ion flow. (4)

(*Total 7 marks*)