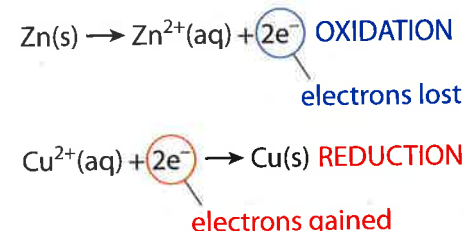# 9 Redox processes

Learning objectives

- Understand the terms oxidation and reduction in terms of the loss/gain of hydrogen/oxygen and the loss/gain of electrons
- Work out oxidation numbers for elements in compounds and ions
- Understand that transition metals and some main group elements can have more than one oxidation number
- Understand how to name compounds and ions using oxidation numbers
- Understand what is meant by a redox reaction
- Understand oxidation and reduction in terms of changes in oxidation numbers
- Work out whether an element has been oxidised or reduced in a given reaction
- Understand what is meant by an oxidising agent and a reducing agent and identify them in reactions

O xidation
I s
L oss of electrons
R eduction
I s
G ain of electrons

Figure 9.1 A mnemonic to help you remember the definition of oxidation and reduction.

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

electrons lost

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

electrons gained

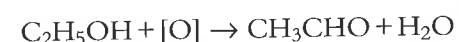**Figure 9.2** Breaking an oxidation–reduction reaction into two half-equations.

9.1 Oxidation and reduction

9.1.1 Definitions

Oxidation and **reduction** may be defined in many ways, such as:

> **Oxidation is the loss of hydrogen or the gain of oxygen, and reduction is the gain of hydrogen or the loss of oxygen.**
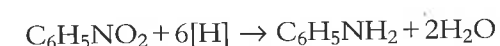
For instance, in the equation:

$$C_2H_5OH + [O] \rightarrow CH_3CHO + H_2O$$

we can see that the C_2H_5OH (ethanol) has been oxidised because it has lost H to form CH_3CHO (ethanal).

> [O] indicates oxygen added in an oxidation reaction.

In the equation:

$$C_6H_5NO_2 + 6[H] \rightarrow C_6H_5NH_2 + 2H_2O$$

$C_6H_5NO_2$ has been reduced because it has lost oxygen/gained hydrogen.

> [H] indicates hydrogen added in a reduction reaction.

These definitions are, however, only useful in a limited number of reactions and a more fundamental definition of oxidation and reduction is:

> **Oxidation – loss of electrons**
> **Reduction – gain of electrons (Figure 9.1)**

For instance, in the reaction:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$
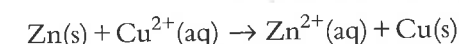
the Zn has been oxidised to Zn^{2+}, because it has lost electrons, and the Cu^{2+} has been reduced to Cu, because it has gained electrons. This can be seen more clearly by splitting the overall reaction into two **half-equations**, as shown in Figure 9.2.

If something loses electrons, something else must gain them, so oxidation and reduction always occur together – if something is oxidised, something else must be reduced. Reactions such as the one described above are called **redox reactions**, indicating that both reduction and oxidation occur.

Although it is fairly easy to understand which species has been oxidised and which reduced in ionic equations such as $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$, it is more difficult to see just where electrons are being transferred in redox reactions such as $PCl_3 + Cl_2 \rightarrow PCl_5$. For discussing reactions such as these in terms of oxidation and reduction, we use the concept of **oxidation number** (oxidation state).

Oxidation number

Oxidation number is a purely formal concept, which regards all compounds as ionic and assigns charges to the components accordingly. It provides a guide to the distribution of electrons and relative charges on atoms in covalent compounds and allows us to understand redox processes more easily.

There are some general rules for working out oxidation numbers.

1. Treat the compound as totally ionic (if the compound is ionic then the charges on the ions are the oxidation numbers). So, CH_4 is a covalent compound but we assign oxidation numbers of -4 for C and $+1$ for H as if it were ionic. KCl is an ionic compound and the oxidation numbers are $+1$ for K and -1 for Cl, which correspond to the charges on the ions.
2. The most electronegative atom in a molecule is assigned a negative oxidation number according to how many electrons it needs to gain to have a full outer shell (see Table 9.1). So in H_2O, oxygen is the more electronegative element and because an oxygen atom has six electrons in its outer shell it needs to gain two electrons to have a full outer shell, therefore the oxidation number of O in H_2O is -2.
3. Assign oxidation numbers accordingly to give the overall charge on the molecule/ion – the sum of the oxidation numbers, taking into account signs and coefficients, is equal to the overall charge on the molecule/ion.
4. The oxidation number of atoms in an element is zero – so the oxidation number of oxygen in O_2 is 0.
5. The elements in groups 1 and 2 virtually always have the group number as their oxidation number.
6. The maximum possible oxidation number for an element will be its group number for elements in groups 1 and 2 and the group number -10 for elements in groups 13–17 (see Table 9.2). It is not possible to lose more electrons than there are in the outer shell – the maximum possible oxidation number for a group 16 element is $+6$ because there are six electrons in the outer shell.

Exam tip
Oxidation number is written with the sign first, e.g. -2, but a charge is written with the number first, e.g. $2-$. This may seem like a trivial point, but if you get it the wrong way round you could lose a mark in the exam!

Atom	Ionic charge	Oxidation number	Comment
F	F^-	-1	always, as most electronegative element
O	O^{2-}	-2	virtually always, but not in compounds with F or in peroxides and superoxides
Cl	Cl^-	-1	not in compounds with O and F; other oxidation numbers include $+1$, $+3$, $+5$, $+7$
H	H^+	$+1$	not in metal hydrides, e.g. NaH, where oxidation number is -1

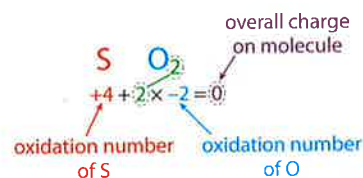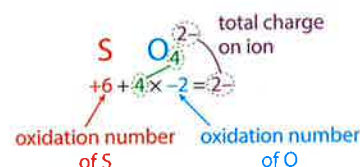**Table 9.1** Assigning charge according to valency.

	Group 1	Group 2	Group 13	Group 14	Group 15	Group 16	Group 17
Maximum oxidation number	$+1$	$+2$	$+3$	$+4$	$+5$	$+6$	$+7$

Table 9.2 The connection between group number and the maximum possible oxidation number.
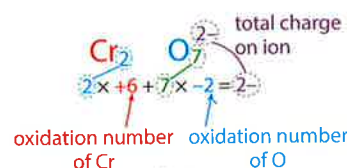
Figure 9.3 Assigning oxidation numbers in sulfur dioxide.

Figure 9.4 Assigning oxidation numbers in the sulfate(VI) ion.

Figure 9.5 Assigning oxidation numbers in the dichromate(VI) ion.

Extension

Superoxides, such as RbO_2, contain the O_2^- ion.

Neutral ligands	1– ligands
H_2O	Cl^-
NH_3	CN^-

Table 9.4 Examples of neutral and negatively charged ligands in transition metals.

Examples

SO_2

Sulfur dioxide is a covalent compound, but we will assign oxidation numbers as if it were an ionic compound. The more electronegative atom is oxygen, and therefore this is assigned its normal valency (the charge it would have in an ionic compound) – the oxidation number of oxygen is -2. The overall charge on the molecule is zero, and therefore the oxidation number of S must be $+4$ to cancel out the total oxidation number of two oxygen atoms (-4) (Figure **9.3**).

SO_4^{2-}

The more electronegative atom is oxygen and therefore this is assigned its normal valency – the oxidation number of oxygen is -2. The total oxidation number of four oxygen atoms is 4×-2, or -8. Because the overall charge on the ion is $2-$, the oxidation number of sulfur must be $+6$ to cancel out all but 2 of the total oxidation number of the four oxygen atoms (Figure **9.4**).

$Cr_2O_7^{2-}$

The more electronegative atom is oxygen and therefore the oxidation number of oxygen is -2. The total oxidation number of seven oxygen atoms is 7×-2, or -14. Because the overall charge on the ion is $2-$, the total oxidation number of two chromium atoms must be $+12$ to cancel out all but 2 of the total oxidation number of the seven oxygen atoms. Therefore the oxidation number of chromium is $+12/2$, or $+6$ (Figure **9.5**).

Hydrogen peroxide (H_2O_2)

The oxidation number of oxygen cannot be -2 here because the oxidation number of hydrogen would have to be $+2$. This is not possible because hydrogen has only one electron – its maximum oxidation number is $+1$. This means that the oxidation number of hydrogen in H_2O_2 is $+1$ and that of oxygen is -1. There are many ionic peroxides, such as Na_2O_2, which contain the O_2^{2-} ion.

Metal hydrides

Hydrogen forms hydrides with many metals – for example NaH and CaH_2. Hydrogen is more electronegative than metals and so its oxidation number will be -1. For many of these, the bonding is mostly ionic and they can be regarded as containing the H^- ion.

Some other oxidation numbers are shown in Table **9.3**.

Transition metals

The oxidation number of a transition metal in a complex ion is worked out using the charges on the ligands. Ligands may be either neutral or negatively charged – examples of each type are shown in Table **9.4**.

Let us consider $[Fe(H_2O)_6]^{2+}$. All the ligands are neutral, so the overall charge on the ion is just due to the iron and so the oxidation number of iron must be $+2$.

In $[Ni(CN)_4]^{2-}$, all the ligands have a $1-$ charge, so the total charge on all four ligands is $4-$. The overall charge on the ion is $2-$, so the oxidation number of Ni must be $+2$ to cancel out $2-$ from the $4-$ charge.

Oxidation numbers			
SO_3	S: +6		O: −2
PCl_3	P: +3		Cl: −1
Cl_2	Cl: 0		Cl: 0
PO_4^{3-}	P: +5		O: −2
OF_2	O: +2		F: −1
CaO_2	Ca: +2		O: −1
CO_2	C: +4		O: −2
C_2H_6	C: −3		H: +1
LiH	Li : +1		H: −1
CaF_2	Ca: +2		F: −1
HNO_3	H: +1	N: +5	O: −2
H_2SO_4	H: +1	S: +6	O: −2
$KMnO_4$	K: +1	Mn: +7	O: −2
$NaClO_3$	Na: +1	Cl: +5	O: −2

Table 9.3 The oxidation numbers of some elements in a variety of compounds.

Naming compounds using oxidation numbers

SO_2 and SO_3 are commonly called sulfur dioxide and sulfur trioxide, respectively. They are, however, more correctly named using the oxidation number of the sulfur atom. So SO_2 is sulfur(IV) oxide and SO_3 is sulfur(VI) oxide. Strangely enough, no-one ever calls carbon dioxide carbon(IV) oxide or carbon monoxide carbon(II) oxide!

Roman numerals are used for the oxidation numbers in the names of compounds.

The transition metals can have variable oxidation numbers, and so the names of their compounds almost always contain the oxidation number – so $FeCl_2$ is called iron(II) chloride and contains the Fe^{2+} ion, whereas $FeCl_3$ is called iron(III) chloride and contains the Fe^{3+} ion.

Some other names of compounds and ions are shown in Table **9.5**.

CaO_2 is calcium peroxide.

$KMnO_4$ contains the ions K^+ and MnO_4^-.

What exactly are oxidation numbers? The sulfur atom in SO_2 definitely does not have a charge of 4+, so what does the oxidation number actually represent?

Why have scientists developed this systematic way of naming compounds – what has been gained by this? The old name for H_2SO_3 was sulfurous acid and that for $KMnO_4$ was potassium permanganate. Why do some people still prefer to use the old names? Will anything be lost when the old names become obsolete?

Compound/ion	Name
H_2SO_3	sulfuric(IV) acid
H_2SO_4	sulfuric(VI) acid
PCl_3	phosphorus(III) chloride
PCl_5	phosphorus(V) chloride
N_2O	nitrogen(I) oxide
NO_2	nitrogen(IV) oxide
$HClO_3$	chloric(V) acid
PO_4^{3-}	phosphate(V) ion
$CuSO_4$	copper(II) sulfate
SO_4^{2-}	sulfate(VI) ion
$Cr_2O_7^{2-}$	dichromate(VI) ion
CrO_4^{2-}	chromate(VI) ion
MnO_4^{-}	manganate(VII) ion

Table 9.5 These compounds/ions are named systematically using oxidation numbers.

Test yourself

1 Work out oxidation numbers for nitrogen in the following molecules/ions:
 a NF_3 c N_2O e N_2H_4
 b NO d N_2O_4 f NO_2^-

2 Work out the oxidation number of chlorine in the following species:
 a Cl_2O c ClO_4^- e $HClO_3$
 b HCl d ClF_3

3 Work out the oxidation number of the species in bold in each of the following compounds:
 a $\mathbf{Na_2O}$ c $Na_2\mathbf{S}O_3$ e $\mathbf{N}H_4NO_3$
 b $K\mathbf{Br}O_3$ d $K_2\mathbf{Cr}O_4$ f $K\mathbf{H}$

4 Name the following compounds using oxidation numbers:
 a NO c SeO_2 e Cr_2O_3
 b Cl_2O_7 d KIO_3

HL 5 Work out the oxidation number of the transition metal in each of the following complex ions or compounds:
 a $[CuCl_4]^{2-}$ d $[Fe(CN)_6]^{4-}$
 b $[Co(H_2O)_6]^{3+}$ e $[Ag(NH_3)_2]^+$
 c $[MnBr_4]^{2-}$ f $[Co(H_2O)_6]Cl_2$

Oxidation and reduction in terms of oxidation numbers

If an atom gains electrons, its oxidation number will become more negative. Therefore reduction involves a decrease in oxidation number. If an atom loses electrons, its oxidation number increases. Therefore oxidation involves an increase in oxidation number.

We can work out which species is oxidised or reduced in a redox reaction by analysing the oxidation numbers of the substances involved in the reaction.

Examples

$Br_2 + SO_2 + 2H_2O \rightarrow H_2SO_4 + 2HBr$
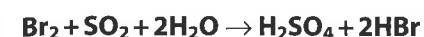
Br_2 is reduced, because its oxidation number decreases from 0 to -1. The sulfur in SO_2 is oxidised because its oxidation number increases from $+4$ to $+6$ (Figure **9.6**). We would usually say that the SO_2 is oxidised.

$6OH^- + 3Cl_2 \rightarrow 5Cl^- + ClO_3^- + 3H_2O$

In this reaction, five chlorine atoms have been reduced but one has been oxidised – therefore Cl_2 has been oxidised and reduced (Figure **9.7**). This type of reaction, in which the same species has been oxidised *and* reduced, is called a **disproportionation** reaction.

$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$
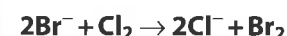
The oxidation number of Cr on both sides of the equation is $+6$, and no other atom undergoes a change in oxidation number. This reaction is, therefore, not a redox reaction.

Figure 9.6 Reduction of Br_2 and oxidation of sulfur.

Figure 9.7 Oxidation and reduction of Cl_2, an example of a disproportionation reaction.

Oxidising and reducing agents

An oxidising agent is a substance that oxidises something else. A reducing agent is a substance that reduces something else.

Examples

$2Br^- + Cl_2 \rightarrow 2Cl^- + Br_2$

Cl_2 is the oxidising agent, because it oxidises the Br^- to Br_2. In terms of electrons, an oxidising agent oxidises a substance by removing electrons from it – here the Cl_2 removes electrons from the bromide ions, oxidising them. The Cl_2 has gained electrons and has been reduced.

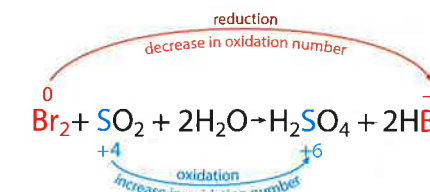The Br^- in this reaction causes the Cl_2 to be reduced by giving electrons to it to form Cl^- – the Br^- acts as a reducing agent in this reaction. The Br^- ions have lost electrons and been oxidised.

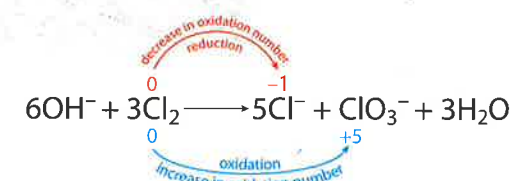**$Cr_2O_7^{2-}(aq) + 6Fe^{2+}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$**

The Fe^{2+} is oxidised to Fe^{3+} by the $Cr_2O_7^{2-}$, so $Cr_2O_7^{2-}$ is the oxidising agent. We can tell that $Cr_2O_7^{2-}$ is the oxidising agent because it has been reduced in the reaction. The $Cr_2O_7^{2-}$ has been reduced by the Fe^{2+}, which means that Fe^{2+} is the reducing agent. We can tell that Fe^{2+} is a reducing agent because it has been oxidised.

Nature of science

Scientific knowledge is constantly changing and evolving and, wherever possible, scientists aim to make models/theories as fundamental and all-encompassing as possible. The original idea of defining oxidation and reduction in terms of oxygen and hydrogen has been broadened to include other reactions. The model of oxidation and reduction in terms of electrons is more fundamental than that in terms of oxygen/hydrogen loss/gain.

Test yourself

6 State whether each of the following half-equations involves oxidation or reduction:

a $Cl_2 + 2e^- \rightarrow 2Cl^-$

b $Mn^{3+} + e^- \rightarrow Mn^{2+}$

c $Cu^+ \rightarrow Cu^{2+} + e^-$

d $I_2 + 6H_2O \rightarrow 2IO_3^- + 12H^+ + 10e^-$

e $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
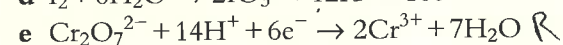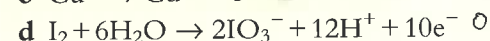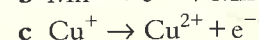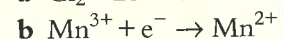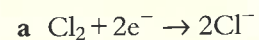
7 State which of the following reactions are redox reactions. For each redox reaction identify the element that has been oxidised and the element that has been reduced.

a $Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$

b $2ZnS + 3O_2 \rightarrow 2ZnO + SO_2$

c $2Na + 2H_2O \rightarrow 2NaOH + H_2$

d $SO_3 + H_2O \rightarrow H_2SO_4$

e $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$

f $2FeSO_4 + H_2SO_4 + H_2O_2 \rightarrow Fe_2(SO_4)_3 + 2H_2O$

g $3HgSO_4 \rightarrow Hg_2SO_4 + Hg + 2SO_2 + 2O_2$

h $2I^- + H^+ + HOCl \rightarrow I_2 + H_2O + Cl^-$
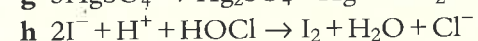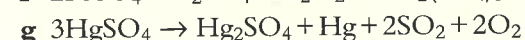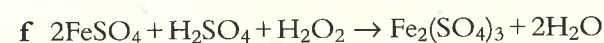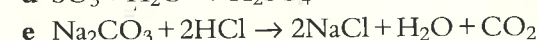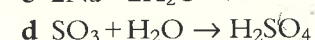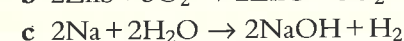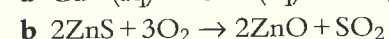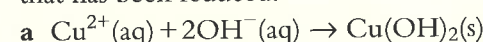
8 In each of the following redox reactions, identify the oxidising agent and the reducing agent:

a $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$

b $Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$

c $I_2O_5 + 5CO \rightarrow 5CO_2 + I_2$

d $S + 6HNO_3 \rightarrow 2H_2O + H_2SO_4 + 6NO_2$

e $2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$

f $2KMnO_4 + 5Na_2C_2O_4 + 8H_2SO_4$
$\rightarrow 2MnSO_4 + 10CO_2 + K_2SO_4$
$+ 5Na_2SO_4 + 8H_2O$

g $6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4$
$\rightarrow 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$
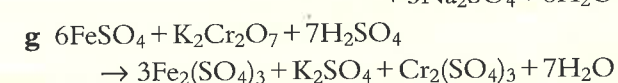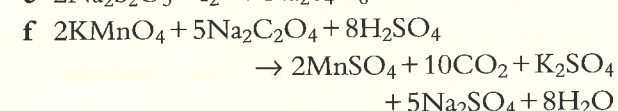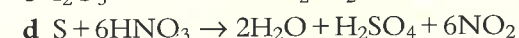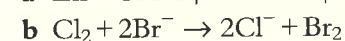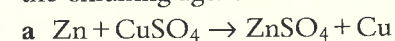
Learning objectives

- Understand what is meant by half-equations and be able to balance them
- Combine half-equations to produce an overall redox equation
- Balance redox equations in acidic or neutral solution using half-equations

The number of electrons is the same in both half-equations.

9.1.2 Redox equations

Half-equations

As already mentioned, a redox equation may be broken down into two half-equations. These half-equations show the oxidation and reduction processes separately. For instance, from the equation:

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

we can separate two processes:

$2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$ **oxidation**

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

Examples

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

This reaction can be separated as:

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

$6Fe^{2+}(aq) \rightarrow 6Fe^{3+}(aq) + 6e^-$ **oxidation**

This second half-equation can be simplified to:

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$ **oxidation**

$Br_2 + SO_2 + 2H_2O \rightarrow H_2SO_4 + 2HBr$

This reaction can be separated as:

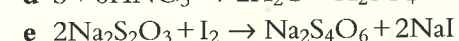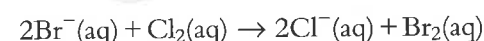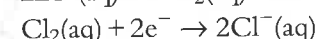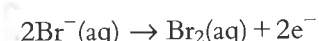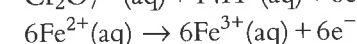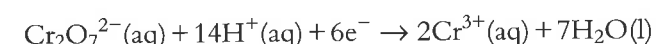$Br_2 + 2H^+ + 2e^- \rightarrow 2HBr$ **reduction**

$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H^+ + 2e^-$ **oxidation**

It can be seen that all these half-equations balance, both in terms of number of atoms on both sides and the total charge on both sides. This must be true for all half-equations.

It should also be noted that the number of electrons lost in the oxidation reaction is equal to the number of electrons gained in the reduction reaction. This must be true because electrons cannot simply disappear or be created from nothing.

Although $2H^+$ and $2e^-$ are required to balance the individual half-equations, both cancel out when the half-equations are combined to give the overall redox equation.

Balancing half-equations in neutral solution

Half-equations must balanced in terms of the number of atoms on both sides and in terms of the total charge on both sides. In some cases it is very straightforward to balance half-equations, and electrons must simply be added to one side or the other.

For example, consider the half-equation:

$$Ni^{2+} \rightarrow Ni$$
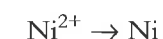
Although the number of nickel atoms on each side is the same, the total charge on the left-hand side is 2+ but the total charge on the right-hand side is 0. In order to balance the charges, we must add $2e^-$ to the left-hand side:

$$Ni^{2+} + 2e^- \rightarrow Ni$$
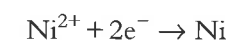
Now the number of atoms and the charges balance on each side.

Now, let's look at another half-equation:

$$Br_2 \rightarrow Br^-$$
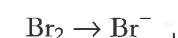
In this example, neither the number of atoms nor the total charge balance. First of all we balance the atoms to get:

$$Br_2 \rightarrow 2Br^-$$
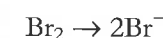
The total charge on the left-hand side is zero, but that on the right-hand side is 2−. To balance the charges we need to add $2e^-$ to the left-hand side so that the charge is equal on both sides:

$$Br_2 + 2e^- \rightarrow 2Br^-$$
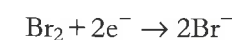
This is now balanced.

These were fairly straightforward examples, but the process becomes a bit more difficult in some cases – we will now consider balancing more complex half-equations for reactions in acidic solution.

Balancing half-equations in acidic solution

The following procedure should be followed for balancing these equations.
1 Balance all atoms except H and O.
2 Add H_2O to the side deficient in O to balance O.
3 Add H^+ to the side deficient in H to balance H.
4 Add e^- to the side deficient in negative charge to balance charge.

Examples

$Cr_2O_7{}^{2-} \rightarrow Cr^{3+}$
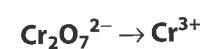
1 Balance all atoms except H and O – the Cr atoms must be balanced:

$$Cr_2O_7{}^{2-} \rightarrow 2Cr^{3+}$$
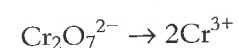
2 Add H_2O to the side deficient in O to balance O – there are 7O atoms on the left-hand side and none on the right-hand side, so $7H_2O$ must be added to the right-hand side:

$$Cr_2O_7{}^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$
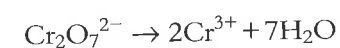
3 Add H^+ to the side deficient in H to balance H – there are 14H atoms on the right-hand side but none on the left-hand side, so $14H^+$ must be added to the left-hand side:

$$Cr_2O_7{}^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$$
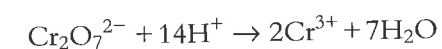
4 Add e^- to the side deficient in negative charge to balance the charge – the total charge on the left-hand side is $2- + 14+ = 12+$, and the total charge on the right-hand side is $2 \times 3+ = 6+$, so $6e^-$ must be added to the left-hand side to balance the charges:

$$Cr_2O_7{}^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
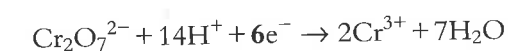
The total charge on the left-hand side is now $2- + 14+ + 6- = 6+$, which is equal to the total charge on the right-hand side.

$S_4O_6{}^{2-} + H_2O \rightarrow H_2SO_3 + H^+ + e^-$
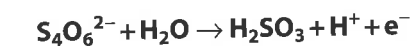
In this case the H_2O, H^+ and e^- have already been included on their correct sides. However, the overall process of balancing the equation is the same.
1 There are 4 S atoms on the left-hand side but only one on the right-hand side, so H_2SO_3 must be multiplied by 4:

$$S_4O_6{}^{2-} + H_2O \rightarrow 4H_2SO_3 + H^+ + e^-$$
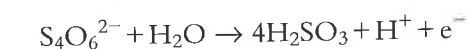
2 There are 7 O atoms on the left-hand side and 12 on the right-hand side, so another 5 H_2O must be added to the left-hand side:

$$S_4O_6{}^{2-} + 6H_2O \rightarrow 4H_2SO_3 + H^+ + e^-$$
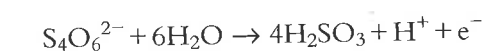
3 There are 12 H atoms on the left-hand side and 9 on the right-hand side, so another 3 H^+ must be added to the right-hand side:

$$S_4O_6{}^{2-} + 6H_2O \rightarrow 4H_2SO_3 + 4H^+ + e^-$$
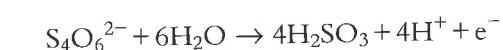
There are now 12 O atoms on each side.

There are now 12 H atoms on each side.

4 The total charge on the left-hand side is 2− and the total charge on the right-hand side is $4 \times 1+ + 1- = 3+$, so five more e^- must be added to the right-hand side to give a total of $6e^-$ on that side to balance the charges:

$$S_4O_6{}^{2-} + 6H_2O \rightarrow 4H_2SO_3 + 4H^+ + 6e^-$$
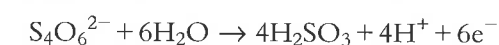
The total charge on both sides is now 2−.

Combining half-equations to produce an overall redox equation

An oxidation half-equation may be combined with a reduction half-equation to produce an overall redox equation. When the half-equations are combined, the number of electrons lost in the oxidation reaction must be the same as the number gained in the reduction reaction.
Let us consider the two half-equations:

$$MnO_4{}^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l) \qquad \textbf{reduction}$$
$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^- \qquad \textbf{oxidation}$$
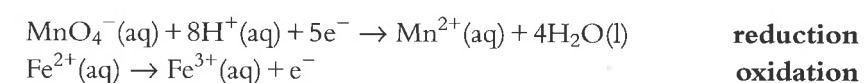
Five electrons are gained in the reduction half-equation, but only one is lost in the oxidation half-equation. The oxidation half-equation must therefore be multiplied by 5:
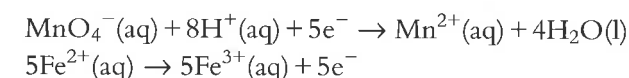
$$MnO_4{}^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$
$$5Fe^{2+}(aq) \rightarrow 5Fe^{3+}(aq) + 5e^-$$

The number of electrons now balance and the two half-equations can be added together:

$$MnO_4{}^-(aq) + 8H^+(aq) + \mathbf{5e^-} \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$
$$5Fe^{2+}(aq) \rightarrow 5Fe^{3+}(aq) + \mathbf{5e^-}$$
$$\overline{MnO_4{}^-(aq) + 8H^+(aq) + \mathbf{5e^-} + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq) + \mathbf{5e^-}}$$
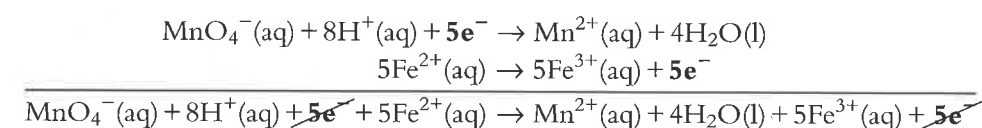
The electrons cancel from each side to give the overall redox equation:
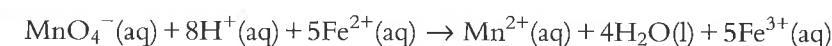
$$MnO_4{}^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$$

A final check can be done to see that this is indeed balanced by checking that the number of atoms of each type is the same on both sides and also that the total charge is the same on both sides.

Exam tip
Overall redox equations never contain electrons – only half-equations have electrons.

Worked example

9.1 What is the overall redox equation when the following two half-equations are combined?

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l) \qquad \text{reduction}$$
$$Re^{3+}(aq) + 4H_2O(l) \rightarrow ReO_4^{2-}(aq) + 8H^+(aq) + 3e^- \qquad \text{oxidation}$$

Five electrons are gained in the reduction half-equation, but only three are lost in the oxidation half-equation. Therefore, in order to balance the number of electrons lost with the number of electrons gained, the oxidation half-equation must be multiplied by 5 and the reduction half-equation by 3:

$$3MnO_4^-(aq) + 24H^+(aq) + \mathbf{15e^-} \rightarrow 3Mn^{2+}(aq) + 12H_2O(l)$$
$$5Re^{3+}(aq) + 20H_2O(l) \rightarrow 5ReO_4^{2-}(aq) + 40H^+(aq) + \mathbf{15e^-}$$

The numbers of electrons now balance and the two half-equations can be added together:

$$3MnO_4^-(aq) + 24H^+(aq) + \mathbf{15e^-} \rightarrow 3Mn^{2+}(aq) + 12H_2O(l)$$
$$5Re^{3+}(aq) + 20H_2O(l) \rightarrow 5ReO_4^{2-}(aq) + 40H^+(aq) + \mathbf{15e^-}$$
$$\overline{5Re^{3+}(aq) + 20H_2O(l) + 3MnO_4^-(aq) + 24H^+(aq) + \cancel{15e^-} \rightarrow 3Mn^{2+}(aq) + 12H_2O(l) + 5ReO_4^{2-}(aq) + 40H^+(aq) + \cancel{15e^-}}$$

The electrons are cancelled from each side to give:

$$5Re^{3+}(aq) + 20H_2O(l) + 3MnO_4^-(aq) + 24H^+(aq) \rightarrow 3Mn^{2+}(aq) + 12H_2O(l) + 5ReO_4^{2-}(aq) + 40H^+(aq)$$

It can be seen that there are H_2O molecules and H^+ ions on both sides. These can also be cancelled to give:

$$5Re^{3+}(aq) + 8H_2O(l) + 3MnO_4^-(aq) \rightarrow 3Mn^{2+}(aq) + 5ReO_4^{2-}(aq) + 16H^+(aq)$$
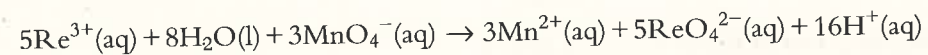
This is the final redox equation.

Balancing redox equations for reactions in acidic or neutral solution

We can combine the above techniques to balance overall redox equations. The equation is first split up into two half-equations which are balanced separately and then combined to give the overall redox equation.

The procedure for doing this is as follows.

1 Separate the reaction equation into oxidation and reduction half-equations.
2 Balance each half-equation separately.
3 Combine the two half-equations after multiplying by the appropriate numbers to balance the electrons in each.
4 Subtract any duplications on left- and right-hand sides.

Example

$$\mathbf{MnO_4^-(aq) + C_2O_4^{2-}(aq) \rightarrow CO_2(g) + Mn^{2+}(aq)}$$

Balance the above redox reaction equation, which happens in acidic solution.
The two half-equations are:

$$MnO_4^-(aq) \rightarrow Mn^{2+}(aq) \qquad\qquad C_2O_4^{2-}(aq) \rightarrow CO_2(g)$$
$$\text{reduction} \qquad\qquad\qquad\qquad \text{oxidation}$$

1 Balance all atoms except H and O:
$$MnO_4^- \rightarrow Mn^{2+} \qquad\qquad C_2O_4^{2-} \rightarrow 2CO_2$$

2 Add H_2O to side deficient in O to balance O:
$$MnO_4^- \rightarrow Mn^{2+} + 4H_2O \qquad\qquad C_2O_4^{2-} \rightarrow 2CO_2$$

3 Add H^+ to side deficient in H to balance H:
$$MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O \qquad\qquad C_2O_4^{2-} \rightarrow 2CO_2$$

4 Add e^- to the side deficient in negative charge to balance charge:
$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \qquad\qquad C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$$

5 These must be combined so that the electrons balance. This is achieved by multiplying the reduction half-equation by 2 and the oxidation half-equation by 5:
$$2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O \qquad\qquad 5C_2O_4^{2-} \rightarrow 10CO_2 + 10e^-$$

The numbers of electrons now balance. The two half-equations are added together and the electrons cancelled:

$$2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O(l)$$
$$5C_2O_4^{2-} \rightarrow 10CO_2 + 10e^-$$
$$\overline{5C_2O_4^{2-}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)}$$
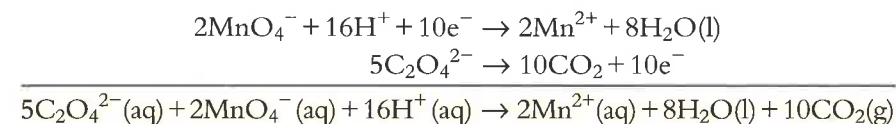
There are no species the same on both sides, so this is the final equation.

Worked example

9.2 Balance the redox equation: $HAsO_2(aq) + BrO_3^-(aq) \rightarrow Br_2(aq) + H_3AsO_4(aq)$

The two half-equations are:
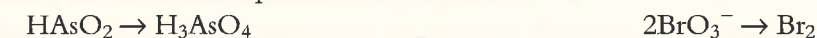
$$HAsO_2(aq) \rightarrow H_3AsO_4(aq) \qquad\qquad BrO_3^-(aq) \rightarrow Br_2(aq)$$

1 Balance all atoms except H and O:
$$HAsO_2 \rightarrow H_3AsO_4 \qquad\qquad 2BrO_3^- \rightarrow Br_2$$

2 Add H_2O to the side deficient in O to balance O:
$$2H_2O + HAsO_2 \rightarrow H_3AsO_4 \qquad\qquad 2BrO_3^- \rightarrow Br_2 + 6H_2O$$

3 Add H^+ to the side deficient in H to balance H:
$$2H_2O + HAsO_2 \rightarrow H_3AsO_4 + 2H^+ \qquad\qquad 2BrO_3^- + 12H^+ \rightarrow Br_2 + 6H_2O$$

4 Add e^- to the side deficient in negative charge to balance charge:
$$2H_2O + HAsO_2 \rightarrow H_3AsO_4 + 2H^+ + 2e^- \qquad\qquad 2BrO_3^- + 12H^+ + 10e^- \rightarrow Br_2 + 6H_2O$$

5 Multiply by 5: $\qquad\qquad\qquad\qquad\qquad$ Multiply by 1:
$$10H_2O + 5HAsO_2 \rightarrow 5H_3AsO_4 + 10H^+ + 10e^- \qquad 2BrO_3^- + 12H^+ + 10e^- \rightarrow Br_2 + 6H_2O$$
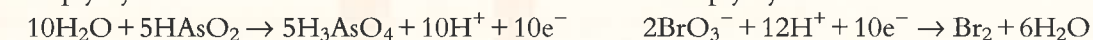
The two half-equations can now be added together and the electrons cancelled:

$$10H_2O + 5HAsO_2 \rightarrow 5H_3AsO_4 + 10H^+ + 10e^-$$
$$2BrO_3^- + 12H^+ + 10e^- \rightarrow Br_2 + 6H_2O$$
$$\overline{10H_2O + 5HAsO_2 + 2BrO_3^- + 12H^+ \rightarrow 5H_3AsO_4 + 10H^+ + Br_2 + 6H_2O}$$
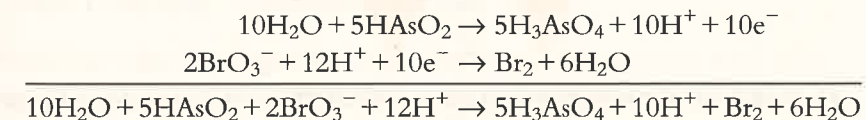
There are H_2O molecules and H^+ ions on both sides, and these can be cancelled to give the overall equation:
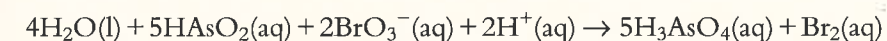
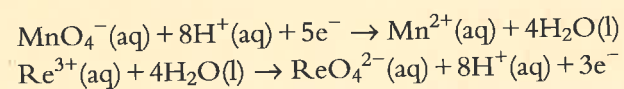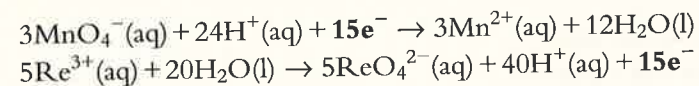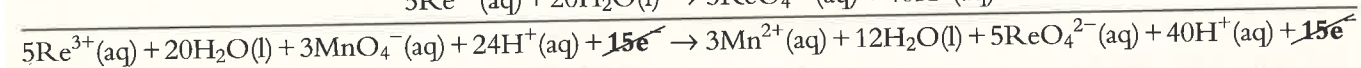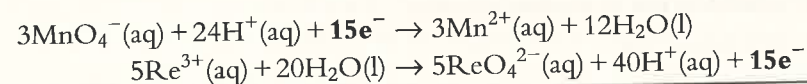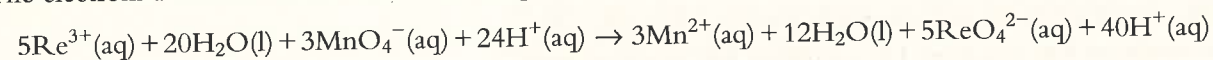$$4H_2O(l) + 5HAsO_2(aq) + 2BrO_3^-(aq) + 2H^+(aq) \rightarrow 5H_3AsO_4(aq) + Br_2(aq)$$

A final check can be done to see that this is, indeed, balanced by checking that the number of atoms of each type is the same on both sides and also that the total charge is the same on both sides.

? Test yourself

9 Balance the following half-equations for reactions that occur in neutral solution:
  a $Fe^{3+} \rightarrow Fe$
  b $Pb^{2+} \rightarrow Pb^{4+}$
  c $I_2 \rightarrow I^-$
  d $S_2O_3^{2-} \rightarrow S_4O_6^{2-}$
  e $C_2O_4^{2-} \rightarrow CO_2$

10 Balance the following half-equations for reactions that occur in acidic solution:
  a $I_2 + H_2O \rightarrow OI^- + H^+ + e^-$
  b $MnO_4^- + H^+ + e^- \rightarrow MnO_2 + H_2O$
  c $IO_3^- + H^+ + e^- \rightarrow I_2 + H_2O$
  d $N_2 + H_2O \rightarrow NO_3^- + H^+ + e^-$
  e $SO_4^{2-} + H^+ + e^- \rightarrow H_2SO_3 + H_2O$

11 Balance the following half-equations for reactions that occur in acidic solution:
  a $VO^{2+} \rightarrow V^{3+}$
  b $Xe \rightarrow XeO_3$
  c $NO_3^- \rightarrow NO$
  d $NO_3^- \rightarrow N_2O$
  e $VO_2^+ \rightarrow VO^{2+}$

12 Balance the following redox equations for reactions that occur in neutral solution:
  a $Cl_2 + Br^- \rightarrow Cl^- + Br_2$
  b $Zn + Ag^+ \rightarrow Zn^{2+} + Ag$
  c $Fe^{3+} + I^- \rightarrow Fe^{2+} + I_2$

13 Balance the following redox equations for reactions that occur in acidic solution:
  a $Fe^{2+} + Cr_2O_7^{2-} + H^+ \rightarrow Fe^{3+} + Cr^{3+} + H_2O$
  b $I^- + Cr_2O_7^{2-} + H^+ \rightarrow I_2 + Cr^{3+} + H_2O$
  c $Zn + VO^{2+} + H^+ \rightarrow V^{3+} + H_2O + Zn^{2+}$
  d $BrO_3^- + I^- \rightarrow Br_2 + I_2$
  e $NpO_2^{2+} + U^{4+} \rightarrow NpO_2^+ + UO_2^+$

Learning objectives

- Understand that metals can be arranged in an activity series according to how easily they can be oxidised
- Use the activity series to predict the feasibility of a redox reaction

9.1.3 The activity series

Metals can be arranged in an activity series (Figure **9.8**).

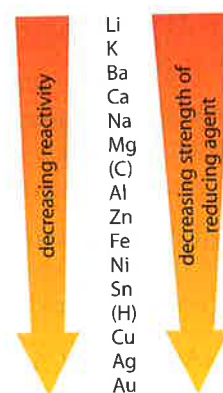> The metals in the activity series are arranged in order of how easily they are oxidised to form positive ions.

Figure 9.8 Activity series showing common metals. Carbon and hydrogen, although non-metals, are often included in the activity series.

Metals higher up the series form positive ions more easily and so are more reactive. Another way of saying this is that the metals higher up in the series lose electrons more readily and are stronger reducing agents.

Extension

Lithium appears to be in the wrong place in this series – if you consider ionisation energies, it is easier to remove an electron from a potassium atom (it is bigger) than from a lithium atom. However, the activity series is arranged in terms of the ease of formation of aqueous ions and so the reaction $Li(s) \rightarrow Li^+(aq) + e^-$ is more favourable than $K(s) \rightarrow K^+(aq) + e^-$ because the Li^+ ion is much smaller than the K^+ ion and so has a much higher enthalpy change of hydration.

Predicting reactions using the activity series

The metals high in the activity series displace those lower in the series from solutions of their salts. For instance, when a piece of zinc is put in a solution containing copper(II) ions, the zinc becomes coated with copper; the blue colour of the solution fades and the solution gets warmer (Figure **9.9**).

Zinc is more readily oxidised than copper (more reactive than copper) and therefore displaces copper ions from solution. The reaction that occurs is:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$
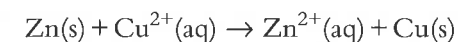
The zinc reduces the copper ions – Zn is a stronger reducing agent than Cu and is therefore able to reduce $Cu^{2+}(aq)$ ions.

Metals higher in the activity series are stronger reducing agents than metals lower in the series. So magnesium will reduce Zn^{2+} ions, zinc will reduce Fe^{2+} ions, iron will reduce Ni^{2+} ions and so on.

Metals above hydrogen in the activity series are stronger reducing agents than hydrogen and should reduce hydrogen ions to hydrogen gas. The reaction between magnesium and hydrogen ions is:

$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$$
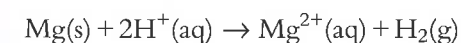
Acids release hydrogen ions in solution, so we can predict that metals above hydrogen in the series should liberate hydrogen gas when mixed with an acid – for example:

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$
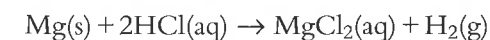
Metals lower than hydrogen in the activity series will not react with acids – copper and silver, for example, do not react with hydrochloric acid.
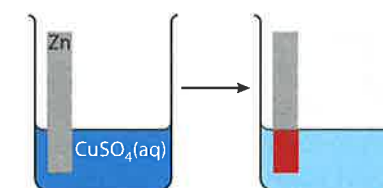
Figure 9.9 Zinc displaces copper from solution – this is called a displacement reaction or a single replacement reaction.

The amount of oxygen needed for fish to survive depends on the type of fish and the temperature. In summer, certain fish will not survive when the dissolved oxygen level falls below $6\,mg\,dm^{-3}$; if it drops below about $3\,mg\,dm^{-3}$ few fish are able to survive. The oxygen concentration needed for fish to survive is substantially higher at higher temperatures. During winter, certain fish may survive down to levels around $0.25\,mg\,dm^{-3}$.

9.1.4 Redox titrations

We met a redox titration earlier – in the worked example involving 'Linked reactions' on page **49**.

A common reaction in problems involving redox titrations is that between thiosulfate ions and iodine to determine the concentration of iodine in a sample:

$$I_2(aq) + 2S_2O_3{}^{2-}(aq) \rightarrow S_4O_6{}^{2-}(aq) + 2I^-(aq)$$
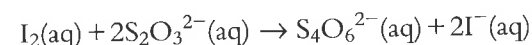
The thiosulfate ion ($S_2O_3{}^{2-}$) is oxidised and the 'average' oxidation number of sulfur changes from +2 in the thiosulfate ion to +2.5 in the tetrathionate ion ($S_4O_6{}^{2-}$). Sulfur is given a fractional oxidation number here because not all the sulfur atoms have the same oxidation number; +2.5 is an average.

Dissolved oxygen

The concentration of dissolved oxygen in water at $20\,°C$ is about $9\,mg\,dm^{-3}$ ($9\,ppm$) – this decreases with increasing temperature. Dissolved oxygen is important in the maintenance of life in aquatic systems. Dissolved oxygen comes from photosynthesis and also from the atmosphere.

Biochemical oxygen demand (also called biological oxygen demand), or BOD for short, is used as a measure of the quality of water. It is a measure of the amount of oxygen used by microorganisms to oxidise the organic matter in the water. Any organic pollutants in river water will be decomposed (oxidised) by **microorganisms** (aerobic bacteria) in the water and this process uses up dissolved oxygen. The higher the BOD, the more organic waste there is in water. If, for instance, sewage is released into a river or lake this will greatly increase the BOD – the water is more polluted. If the water is fast-flowing, new oxygen can be dissolved fairly quickly but this process is much slower in still water.

Organic matter in water might include leaves, animal manure, dead plants and animals. Effluent from water treatment plants will also contain organic matter.

> BOD is defined as the amount of oxygen used by the aerobic microorganisms in water to decompose the organic matter in the water over a fixed period of time (usually 5 days) at a fixed temperature (usually $20\,°C$).

Good-quality river water will have a BOD of less than 1 ppm. Water is generally regarded as unpolluted if it has a BOD lower than 5 ppm. Untreated sewage can have a BOD of 500 ppm but treated sewage from water treatment plants should have a BOD lower than 20 ppm.

The basic principle in measuring BOD is to compare the initial amount of dissolved oxygen in a sample of water with the amount present when the sample has been incubated for 5 days at $20\,°C$. If some water has a dissolved oxygen concentration of 9 ppm, which after incubation for 5 days falls to 4 ppm, the BOD is $9 - 4$, or 5 ppm.

A typical method for determining the amount of dissolved oxygen is the Winkler titration method.

The basic chemistry behind the Winkler method is that manganese(II) sulfate is added to the water and the manganese(II) ions are oxidised under alkaline conditions to manganese(IV) by the oxygen in the water:

$$\underset{\text{manganese(II)}}{2Mn(OH)_2(s)} + O_2(aq) \rightarrow \underset{\text{manganese(IV)}}{2MnO(OH)_2(s)}$$
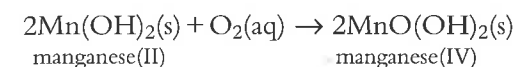
The sample is acidified with sulfuric acid to produce manganese(IV) sulfate:

$$MnO(OH)_2(s) + 4H^+(aq) \rightarrow Mn^{4+}(aq) + 3H_2O(l)$$
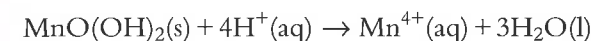
There is no change in oxidation number in this reaction.

Iodide ions are oxidised to I_2 by the manganese(IV) ions:

$$Mn^{4+}(aq) + 2I^-(aq) \rightarrow Mn^{2+}(aq) + I_2(aq)$$
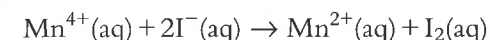
This iodine can then be titrated against a standard sodium thiosulfate solution:

$$I_2(aq) + 2S_2O_3{}^{2-}(aq) \rightarrow S_4O_6{}^{2-}(aq) + 2I^-(aq)$$
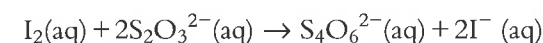
The outcome from these equations is that the number of moles of dissolved oxygen is $\frac{1}{4}$ of the number of moles of sodium thiosulfate used in the titration – or the mass of oxygen is eight times the number of moles of sodium thiosulfate.

There is some disagreement about the reactions involved and an alternative set of equations is:

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

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

$$2S_2O_3{}^{2-}(aq) + I_2(aq) \rightarrow S_4O_6{}^{2-}(aq) + 2I^-(aq)$$
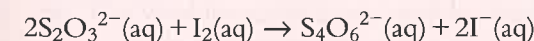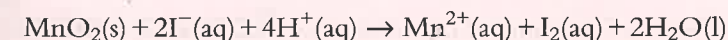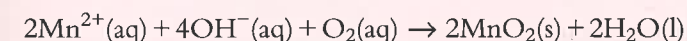
The stoichiometry of these reactions is the same as above.

Nature of science

Science is far from simple and trivial and it can sometimes be extremely difficult to work out exactly what is going on in a chemical reaction. In the reactions shown above it is not even certain that the Mn^{2+} is oxidised to manganese(IV) – it could be oxidised to manganese(III).

Water containing a high proportion of organic matter must be diluted before analysing in a BOD determination.

Manganese(II) sulfate is converted to manganese(II) hydroxide in the presence of hydroxide ions.

Only the manganese(IV) ion is shown here. The equation could also have been written as: $MnO(OH)_2(s) + 2H_2SO_4(aq) \rightarrow Mn(SO_4)_2(aq) + 3H_2O(l)$

Worked example

9.3 The Winkler method was used to measure the concentration of dissolved oxygen in a sample of stream water. Manganese(II) sulfate, sulfuric acid and potassium iodide were added to $100.0\,cm^3$ of water. The iodine that was formed was titrated against a sodium thiosulfate solution with a concentration of $5.00 \times 10^{-3}\,mol\,dm^{-3}$. It was found that $16.00\,cm^3$ of sodium thiosulfate was required for the titration.

The equations for the reactions are:

$$2Mn(OH)_2(s) + O_2(aq) \rightarrow 2MnO(OH)_2(s) \qquad \textbf{equation 1}$$

$$MnO(OH)_2(s) + 4H^+(aq) \rightarrow Mn^{4+}(aq) + 3H_2O(l) \qquad \textbf{equation 2}$$

$$Mn^{4+}(aq) + 2I^-(aq) \rightarrow Mn^{2+}(aq) + I_2(aq) \qquad \textbf{equation 3}$$

$$I_2(aq) + 2S_2O_3{}^{2-}(aq) \rightarrow S_4O_6{}^{2-}(aq) + 2I^-(aq) \qquad \textbf{equation 4}$$

a Calculate the number of moles of sodium thiosulfate used.
b Calculate the number of moles of iodine in the solution.
c Calculate the number of moles of manganese(IV) that produced this amount of I_2.
d Calculate the concentration of dissolved oxygen in $mg\,dm^{-3}$ and in parts per million.
e Another sample of water from the same source was incubated for 5 days at $20\,°C$. At the end of the incubation the Winkler method was used to determine concentration of dissolved oxygen. It was found that the concentration of dissolved oxygen in the sample was $2.20\,mg\,dm^{-3}$. Calculate the biochemical oxygen demand.

a The number of moles of sodium thiosulfate can be calculated using:

no. of moles = volume (in dm^3) × concentration

$$= \left(\frac{16.00}{1000}\right) \times 5.00 \times 10^{-3}$$

$$= 8.00 \times 10^{-5}\,mol$$

b To calculate the number of moles of iodine, we must use equation **4**.

Two moles of thiosulfate ions react with one mole of iodine. The number of moles of iodine is therefore half the number of moles of thiosulfate.

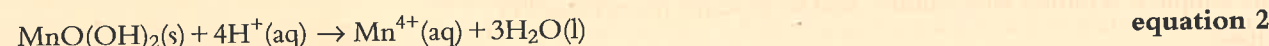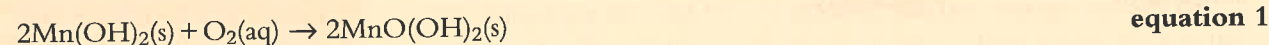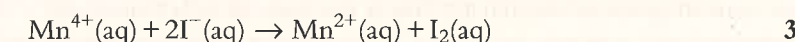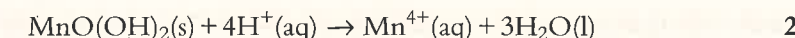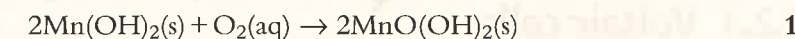$$\text{no. of moles of iodine} = \frac{8.00 \times 10^{-5}}{2} = 4.00 \times 10^{-5}\,mol$$

c The number of moles of manganese(IV) is obtained from equation **3**.

The number of moles of manganese(IV) is the same as the number of moles of I_2.

Number of moles of manganese(IV) is $4.00 \times 10^{-5}\,mol$.

d To determine the number of moles of oxygen we need to use the first three equations:

$$2Mn(OH)_2(s) + O_2(aq) \rightarrow 2MnO(OH)_2(s) \qquad \textbf{1}$$

$$MnO(OH)_2(s) + 4H^+(aq) \rightarrow Mn^{4+}(aq) + 3H_2O(l) \qquad \textbf{2}$$

$$Mn^{4+}(aq) + 2I^-(aq) \rightarrow Mn^{2+}(aq) + I_2(aq) \qquad \textbf{3}$$

The manganese(IV) that reacts in equation **3** is produced in equation **2** – so the number of moles of $Mn^{4+}(aq)$ in equation **2** is $4.00 \times 10^{-5}\,mol$.

From equation **2**, the number of moles of $MnO(OH)_2$ is the same as the number of moles of $Mn^{4+}(aq)$ – so there are $4.00 \times 10^{-5}\,mol\,MnO(OH)_2$.

This number of moles of $MnO(OH)_2$ are produced in equation **1** – therefore the number of moles of $MnO(OH)_2$ in equation **1** is $4.00 \times 10^{-5}\,mol$.

From equation **1** we can see that 1 mol O_2 produces 2 mol $MnO(OH)_2$, so the number of moles of O_2 is half the number of moles of $MnO(OH)_2$. Therefore the no. of moles of oxygen in the sample is $\frac{4.00 \times 10^{-5}}{2}$, that is $2.00 \times 10^{-5}\,mol$.

This is the number of moles of dissolved oxygen in $100.0\,cm^3$, so the number of moles of O_2 in $1.000\,dm^3$ of water is 10 times as much – that is $2.00 \times 10^{-4}\,mol$ and so the concentration of dissolved oxygen in the water is $2.00 \times 10^{-4}\,mol\,dm^{-3}$.

The mass of oxygen present in $1.000\,dm^3$ of water is $2.00 \times 10^{-4} \times 32.00 = 6.40 \times 10^{-3}\,g$

Therefore, we can say that the concentration of oxygen is $6.40 \times 10^{-3}\,g\,dm^{-3}$ or $6.40\,mg\,dm^{-3}$. This is equivalent to $6.40\,ppm$.

e The biochemical oxygen demand is determined by subtracting the final concentration of oxygen from its initial concentration.

$$BOD = 6.40 - 2.20 = 4.20\,mg\,dm^{-3} \text{ or } 4.20\,ppm.$$

? Test yourself

14 The Winkler method was used to measure the concentration of dissolved oxygen in a sample of river water. Manganese(II) sulfate, sulfuric acid and potassium iodide were added to $50.0\,cm^3$ of the water. The iodine that was liberated was titrated against sodium thiosulfate solution with a concentration of $2.00 \times 10^{-3}\,mol\,dm^{-3}$; $25.00\,cm^3$ of sodium thiosulfate was required for the titration.

a Calculate the number of moles of sodium thiosulfate used.
b Calculate the number of moles of iodine present in the solution.
c Calculate the number of moles of manganese(IV) that produced this number of moles of I_2.
d Calculate the concentration of dissolved oxygen in $mg\,dm^{-3}$.
e Another sample of water from the same source was incubated for 5 days at $20\,°C$. At the end of this the Winkler method was used to determine the concentration of dissolved oxygen. It was found that the oxygen concentration in the sample was $4.60\,mg\,dm^{-3}$. Calculate the biochemical oxygen demand and comment on whether the water would be regarded as polluted.

9.2 Electrochemical cells

9.2.1 Voltaic cells

Voltaic cells (galvanic cells) provide us with a way of harnessing redox reactions to generate electricity. This is the basis of cells (batteries).

When a piece of zinc is put into a solution of copper(II) sulfate an exothermic reaction occurs and the zinc becomes coated with copper and the blue colour of the copper sulfate solution fades (Figure **9.9**, page **381**).

The overall reaction is:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$
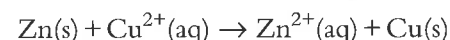
The half-equations involved are:
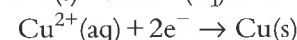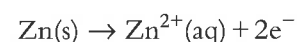
$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad \textbf{oxidation}$$
$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad \textbf{reduction}$$

When zinc metal is added to a solution containing Cu^{2+} ions, electrons are transferred from the zinc to the Cu^{2+} – the Cu^{2+} is reduced and the zinc is oxidised.

However, if the two reactions are separated, as in Figure **9.10**, exactly the same reaction occurs, except that instead of the electrons being transferred directly from the Zn to the Cu^{2+} they are transferred via the external circuit.
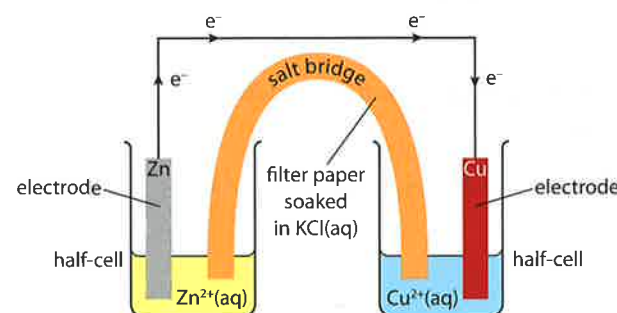
Figure 9.10 A voltaic cell.

In the left-hand beaker, zinc atoms are oxidised to Zn^{2+} ions and the electrons that are lost flow around the circuit to the other beaker, where they are gained by Cu^{2+} ions to form copper. If the reaction were allowed to keep going, we would see the zinc electrode getting smaller (as the zinc goes into solution as Zn^{2+}), the Cu electrode getting larger (as it is coated with copper) and the colour of the solution in the right-hand beaker becoming paler (as copper ions are converted to copper atoms).

The reaction between zinc and copper(II) ions is exothermic but when the two half-reactions are separated in a voltaic cell, instead of chemical energy (internal energy) being converted to heat it is converted to electrical energy which can do useful work – such as drive a motor to lift a mass.

If we put a bulb in the circuit we would see the bulb light up because current flows.

The blue colour of the solution is due to the presence of $Cu^{2+}(aq)$ ions.

Why is a salt bridge necessary?

In the cell shown in Figure **9.10**, current will not flow unless the salt bridge is present. If the salt bridge were not present and the reaction were to proceed, there would be a build up of Zn^{2+} ions in the left-hand beaker, the solution would become positively charged overall and any further oxidation of zinc atoms to Zn^{2+} would be opposed. Similarly, there would be a decrease in the concentration of Cu^{2+} ions in the right-hand beaker which would mean that this solution would have a negative charge and any further reduction of Cu^{2+} ions would be opposed. The flow of electrons from the positively charged half-cell to the negatively charged half-cell would not occur. The salt bridge contains ions that can flow out of the salt bridge into the individual half-cells to prevent any build up of charge (Figure **9.11**). Similarly, any excess ions in the individual half-cells can flow into the salt bridge to prevent any build up of charge.
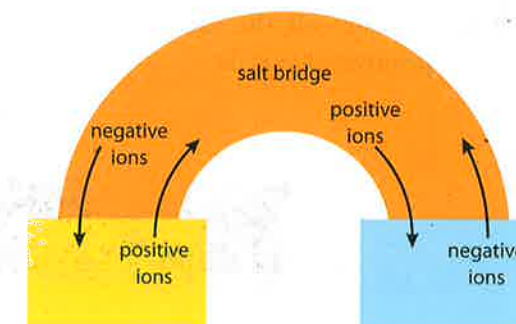
Figure 9.11 Ions flow into and out of the salt bridge to balance the charges in the half-cells.

The **salt bridge** provides an electrical connection between the two half-cells to complete the circuit. It allows ions to flow into or out of the half-cells to balance out the charges in the half-cells.

A salt bridge usually contains a concentrated solution of an ionic salt such as KCl.

Charge flow and the nature of the electrodes

Negative charge always flows in the same continuous direction around a complete circuit – in this case the electrons and the negative ions are all travelling clockwise around the circuit (Figure **9.12**).
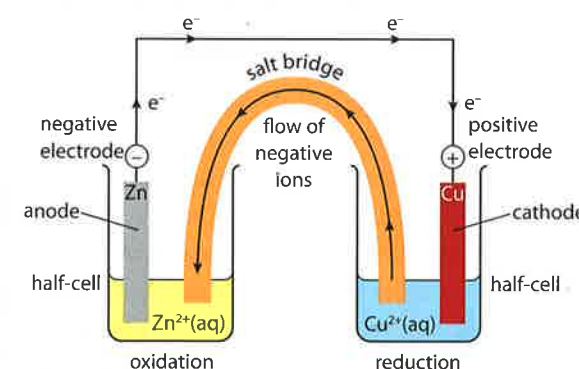
Figure 9.12 Direction of flow of charge. Positive ions flow in the opposite direction through the salt bridge.

In the zinc half-cell, an oxidation reaction occurs:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e-$$
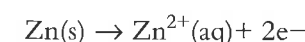
An **anode** is defined as the electrode at which oxidation occurs.

So the zinc electrode is the anode in this cell. Because electrons are released at the zinc electrode, this is the negative electrode.

In the copper half-cell, a reduction reaction occurs:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$
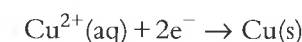
The more reactive metal will have the greater tendency to be oxidised and will be the negative electrode (anode) in a cell.

In a voltaic cell, the anode is the negative electrode.

The cathode is defined as the electrode at which reduction occurs.

So the copper electrode is the cathode in this cell. Because electrons flow through the external circuit towards this electrode, and are used up there, this is the positive electrode.

Cell notation for voltaic cells

Chemists often use a shorthand notation (cell–diagram convention) for describing the reactions that go on in a voltaic cell. The cell discussed above can be written as:

$$Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$$
$$\quad\quad oxidation \quad\quad\quad reduction$$
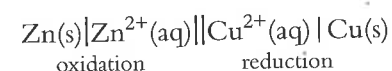
A **single vertical line** represents a phase boundary (between solid and aqueous solution here) and the **double line** indicates the salt bridge. Reading from left to right we can see that Zn is oxidised to Zn^{2+} and that Cu^{2+} is reduced to Cu. The reaction at the anode is shown by convention on the left and that at the cathode on the right.

Any electrodes that the wires are actually joined to are put at the extremes on both sides. For example, some cells are set up using gases or metal ions but no solid metal. In this case we do not have anything that we can physically connect a wire to and so use platinum (a very inert metal) as the electrode (Figure **9.13**).
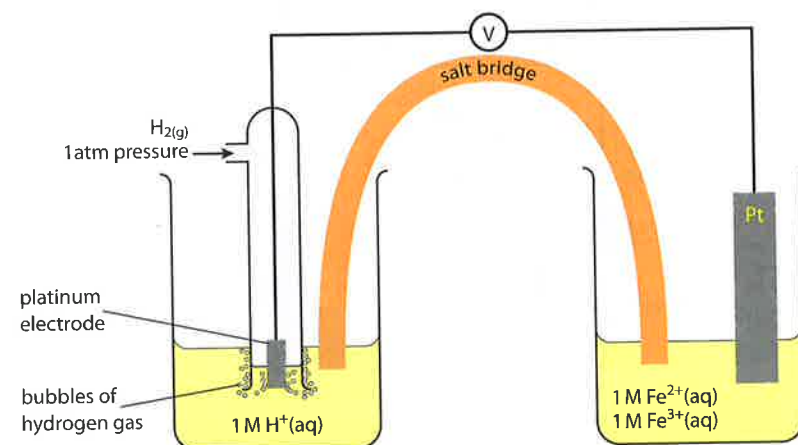
Figure 9.13 A voltaic cell with inert electrodes – the left half-cell involves a standard hydrogen electrode, which is discussed in more detail in the Higher Level section later. (Note: $1\,M = 1\,mol\,dm^{-3}$)

The overall reaction in this cell is:

$$H_2(g) + 2Fe^{3+}(aq) \rightarrow 2H^+(aq) + 2Fe^{2+}(aq)$$
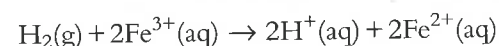
The cell notation can be written as:

$$Pt|H_2(g), H^+(aq)||Fe^{3+}(aq),Fe^{2+}(aq)|Pt$$

Again, the oxidation reaction is written on the left, and the reduction on the right. $Fe^{3+}(aq)$ and $Fe^{2+}(aq)$ are separated by a comma because they are in the same phase (both aqueous solutions). The platinum electrodes are written at the extremes on both sides.

Worked example

9.4 Given the cell notation:

$$Zn(s)|Zn^{2+}(aq)||Fe^{3+}(aq),Fe^{2+}(aq)|Pt$$
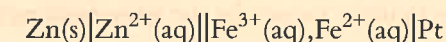
write the half-equations for the reactions that occur in the cell, and hence the overall cell reaction.

The reaction at the anode is on the left-hand side: $Zn(s)|Zn^{2+}(aq)$

We now balance this half-equation by adding electrons:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$ **oxidation**
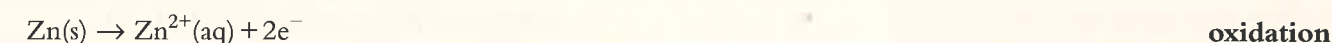
Similarly, we can balance the half-equation for the reaction at the cathode:

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$$ **reduction**

There are two electrons involved in the oxidation half-equation but only one in the reduction half-equation, therefore the reduction half-equation must be multiplied by 2 before combining with the oxidation half-equation for the overall cell reaction:

$$2Fe^{3+}(aq) + Zn(s) \rightarrow 2Fe^{2+}(aq) + Zn^{2+}(aq)$$
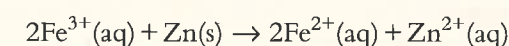
The size of the voltage

If a voltmeter is inserted across the $Zn|Zn^{2+}||Cu^{2+}|Cu$ cell described above, it will read a voltage of just over one volt (Figure **9.14a**). However, if the zinc electrode is replaced by a magnesium electrode, the voltage is much higher (Figure **9.14b**). This is because there is a bigger difference in reactivity between magnesium and copper than between zinc and copper – magnesium and copper are further apart in the activity series than magnesium and zinc. The magnesium has a greater tendency than zinc to donate electrons to copper ions.
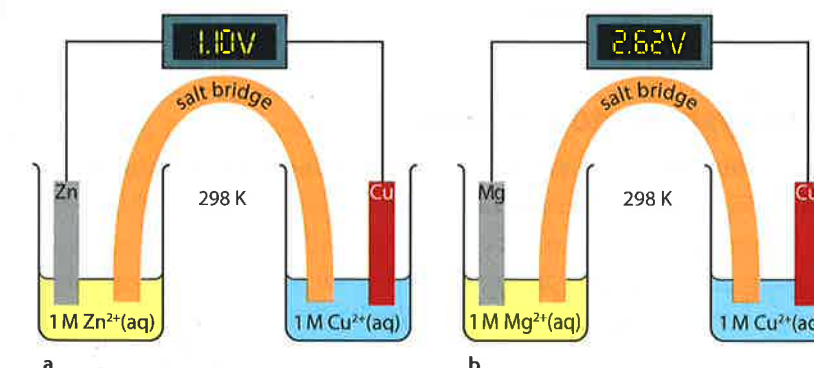
Figure 9.14 a The voltage in a $Zn|Zn^{2+}||Cu^{2+}|Cu$ cell is less than **b** in an $Mg|Mg^{2+}||Cu^{2+}|Cu$ cell. Note: $1\,M = 1\,mol\,dm^{-3}$.

Nature of science

Every year, more and more sophisticated electronic devices are being developed but they all rely on batteries and the development of better batteries is a huge area of research. This research involves collaboration between scientists with different specialisms and involves a great deal of creativity, imagination and investment. This type of scientific research is not, however, carried out for altruistic reasons and one of the main factors that drives this research is the desire to make money by the firms funding it.

? Test yourself

15 Consider four imaginary metals X, Z, A and Q.

  a On the basis of the following data, arrange the metals X, Z and Q in order of reactivity (most reactive first):
- Z reduces Q^{2+} to Q
- X reduces Z^{2+} to Z

  b The following reactions also occur:

$$A + Q^{2+} \rightarrow A^{2+} + Q$$
$$Z + A^{2+} \rightarrow Z^{2+} + A$$

   i Is A a stronger or weaker reducing agent than Q?

   ii Arrange all four metals in order of reducing ability (strongest reducing agent first).

   iii Which of the species, A, A^{2+}, Z, Z^{2+}, Q, Q^{2+}, X, X^{2+} is the strongest oxidising agent?

  c An electrochemical cell is set up with a piece of A dipping into a solution of $A(NO_3)_2$ in one half-cell and a piece of X dipping into a solution of XSO_4 in the other half-cell.

   i Which way do electrons flow in the external circuit?

   ii Which is the anode in the cell?

   iii Write the cell notation for this cell.

   iv The $X|XSO_4$ half-cell is replaced by a $Z|ZSO_4$ half-cell. Will the voltage be higher or lower than that in the original cell?

Learning objectives

- Describe the features of an electrolytic cell
- Understand the differences between an electrolytic cell and a voltaic cell
- Understand how current is conducted during electrolysis
- Predict the products of electrolysis of a molten salt
- Write half-equations for the reactions occurring at the electrodes during electrolysis

9.2.2 Electrolytic cells

Electrolysis is the breaking down of a substance (in molten state or solution) by the passage of electricity through it.

Electrolysis of molten salts

The experimental set-up for the electrolysis of molten lead bromide is shown in Figure 9.15. The overall reaction is:

$$PbBr_2(l) \xrightarrow[\text{energy}]{\text{electrical}} Pb(l) + Br_2(g)$$
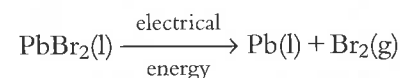
The lead bromide is broken down into its elements, lead and bromine, by the passage of the electricity.

Positive electrode

At the positive electrode, bromide ions are oxidised and lose electrons to form bromine:

$$2Br^-(l) \rightarrow Br_2(g) + 2e^- \qquad \textbf{oxidation}$$

Because oxidation occurs at this electrode, the positive electrode is the anode in an electrolytic cell.

Negative electrode

At the negative electrode, lead ions are reduced as they gain electrons to form lead:

$$Pb^{2+}(l) + 2e^- \rightarrow Pb(l) \qquad \textbf{reduction}$$

Because reduction occurs at this electrode, the negative electrode is the cathode in an electrolytic cell.

Conduction of electricity in an electrolytic cell

In the external circuit, the current is carried by electrons (delocalised electrons in the metal wire) but in the molten salt (electrolyte), conduction involves the movement of **ions** (Figure 9.16).
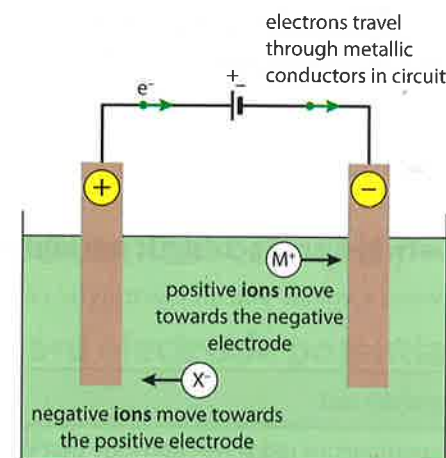
Figure 9.16 Conduction of electricity in an electrolytic cell.

Electrons travel from the negative pole of the battery to the negative electrode. The positive ions in the electrolyte move towards the negative electrode. At the negative electrode, electrons are transferred to the positive ions. The negative ions move towards the positive electrode. At the positive electrode the extra electron(s) from the negative ion is/are transferred to the electrode. The electrons released from the negative ions travel through the external circuit to the positive pole of the battery.

Electrons are taken from the external circuit at the negative electrode (by the positive ions) and given back to the external circuit at the positive electrode (by the negative ions). The circuit is completed, but the electrons that flow into the positive side of the battery are not the ones that flowed out of the negative side of the battery. No electrons travel through the electrolyte.
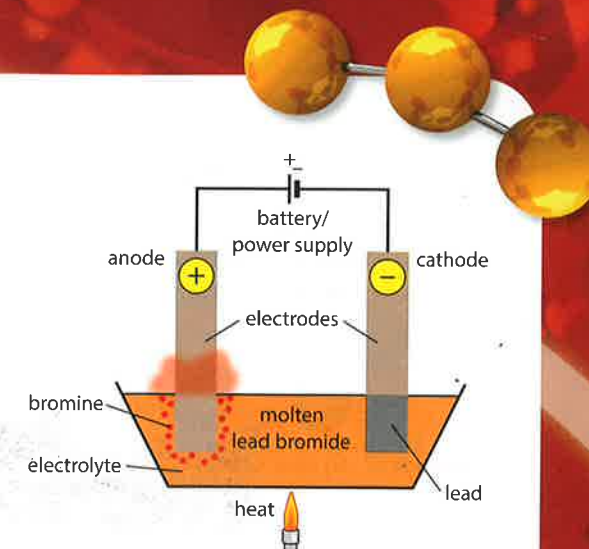
Figure 9.15 The electrolysis of molten lead bromide.

The electrodes are usually made of graphite, a fairly inert non-metal which conducts electricity.

The anode is the electrode at which oxidation occurs.

The cathode is the electrode at which reduction occurs.

Negative electrode:
$$M^+ + e^- \rightarrow M \qquad \text{reduction}$$
Positive electrode:
$$X^- \rightarrow X + e^- \qquad \text{oxidation}$$

An **electrolyte** is a solution or a molten compound that will conduct electricity, with decomposition at the electrodes as it does so. Electrolytes contain ions that are free to move towards the electrodes.
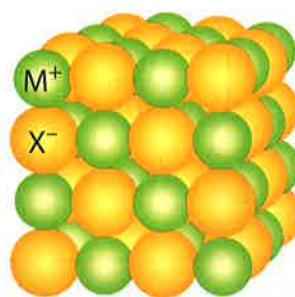
Figure 9.17 An ionic lattice.

Reduction occurs at the cathode.

Oxidation occurs at the anode.

Ionic salts will not conduct electricity when solid because the ions are held tightly in the lattice structure and are therefore not free to move (Figure **9.17**).

The products of electrolysis of a molten salt

When a molten salt is electrolysed, the products at the electrodes are the elements of which that salt is made up. A metal is formed at the negative electrode because metals form positive ions, and a non-metal is formed at the positive electrode because non-metals form negative ions.

Electrolysis of molten aluminium oxide (Al_2O_3)

A metal is formed at the negative electrode (cathode) – in this case, aluminium:

$$Al^{3+} + 3e^- \rightarrow Al \qquad \text{reduction}$$

A non-metal is formed at the positive electrode – in this case, oxygen:

$$2O^{2-} \rightarrow O_2 + 4e^- \qquad \text{oxidation}$$

Electrolysis of molten potassium chloride

Potassium is formed at the negative electrode (cathode) and chlorine is formed at the positive electrode (anode):

$$K^+ + e^- \rightarrow K \qquad \text{reduction}$$
$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad \text{oxidation}$$

The differences between an electrolytic cell and a voltaic cell

The differences between a voltaic and an electrolytic cell are summarised in Table **9.6**.

Voltaic cell	Electrolytic cell
spontaneous redox reaction generates electricity	non-spontaneous redox reaction (one that would not happen by itself) is brought about by the passage of an electric current
conversion of chemical energy to electrical energy	conversion of electrical energy to chemical energy
anode is negative electrode and cathode is positive electrode	anode is positive electrode and cathode is negative electrode

Table 9.6 Comparison of voltaic and electrolytic cells.

? Test yourself

16 State the products at the anode and cathode when the following molten salts are electrolysed:
  a potassium bromide
  b copper(II) chloride
  c nickel(II) oxide
  d calcium chloride

17 Write equations for the reactions at the anode and cathode when the following molten salts are electrolysed:
  a sodium chloride
  b iron(III) oxide
  c magnesium bromide

Iron is the second most abundant metal in the Earth's crust and, because it is not very reactive, it can be extracted relatively easily from its ore by heating with carbon. It has been used since ancient times and, in the form of steel, is the most important construction metal. Mild steel has a very large number of uses, from building bridges to making car bodies. Although iron is not very reactive, it does undergo one very important redox reaction in the presence of air and water – rusting. Rusting of iron structures, machinery, vehicles etc. costs the world's economies billions of dollars each year.
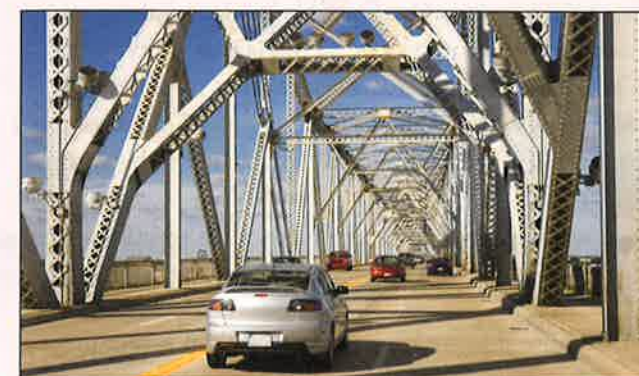
Aluminium is the most abundant metal in the Earth's crust. It is much more reactive than iron and so is more difficult to extract from its compounds. It was not isolated until 1825. The advent of electricity allowed the commercial production of aluminium by electrolysis and has resulted in aluminium replacing iron for many uses. Aluminum has a low density (about one-third the density of iron) and so is useful in aeroplanes, for example. Aluminium is resistant to corrosion because, although it is significantly more reactive than iron, it has an impermeable oxide layer on the surface that prevents further reaction with air.

9.3 Electrochemical cells (HL)

9.3.1 Standard electrode potentials

Cell potentials

The voltmeter in the $Zn|Zn^{2+}||Cu^{2+}|Cu$ cell, shown on page 386, will read $1.10\,V$ if the concentrations of both solutions are $1\,mol\,dm^{-3}$ and the temperature is $298\,K$. This value is called the **standard cell potential** and gives us some idea of the favourability of the redox reaction:

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$
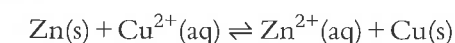
A standard cell potential is the EMF (voltage) produced when two half-cells are connected under standard conditions. This drives the movement of electrons through the external circuit from the negative electrode to the positive electrode.

Learning objectives

- Describe the features of the standard hydrogen electrode
- Understand the terms standard electrode potential and standard cell potential
- Calculate the cell potential for a given redox reaction
- Use the cell potential to predict whether a redox reaction will be spontaneous
- Use standard cell potentials to calculate $\Delta G^\ominus$ for a reaction

EMF stands for 'electromotive force'.

The Zn/Cu^{2+} reaction has been shown with reversible equilibrium arrows above – indeed, $E^{\ominus}$ is related to the equilibrium constant, and this system will reach a state of equilibrium. However, in most cases the position of equilibrium lies a very long way to the right, and the reaction will go essentially to completion – K_c for the Zn/Cu^{2+} system at 298 K is about 1×10^{37}!

A standard cell potential ($E^{\ominus}_{cell}$) is related to the value of $\Delta G^{\ominus}$ and K_c for the reaction. The higher the value (more positive) of the standard cell potential, the more favourable the reaction (ΔG is more negative and the value of K_c is larger).

When the zinc in this cell is replaced by magnesium, the value of the standard cell potential is higher, which indicates that the reaction:

$$Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$$
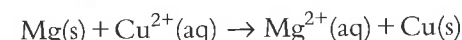
is more favourable (more spontaneous/ΔG is more negative) than the reaction involving zinc (see Figure **9.14**, page **389**). This suggests that Mg has a greater tendency to reduce Cu^{2+} ions than Zn does.

Using different half-cell combinations, we can measure the tendency for different redox reactions to occur and build up the activity series. However, what would be more useful is being able to predict the favourability of a particular redox reaction from a knowledge of the favourability of the individual oxidation and reduction half-reactions making up the redox reaction. This will provide us with a way of predicting in which direction a particular redox reaction will occur and how favourable it will be without setting up each cell physically.
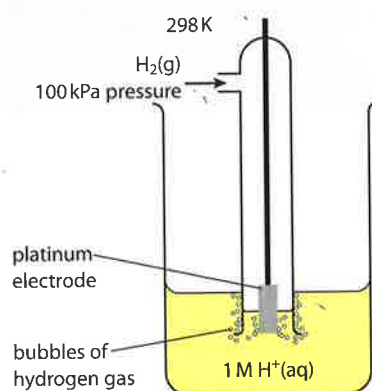
However, it is not possible to measure the tendency for reactions such as:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$
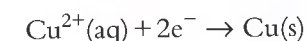
to occur in isolation, because if something is reduced then something else must be oxidised. The tendency of these reactions to occur can be measured only by connecting one half-cell to another half-cell and measuring the cell potential. However, if we always choose one particular half-cell as a reference half-cell in the system, then by measuring the cell potentials of lots of cells relative to this half-cell we will be able to build up a set of values that enables us to judge the relative oxidising and reducing abilities of various species. The reference half-cell that we choose is called the **standard hydrogen electrode**.

The standard hydrogen electrode

Individual half-cell electrode potentials cannot be measured in isolation, and so they are measured relative to a standard. The standard that is chosen is the standard hydrogen electrode (Figure **9.18**).

In the standard hydrogen electrode, hydrogen gas at 100 kPa (1 bar) pressure is bubbled around a platinum electrode of very high surface area in a solution of H^+ ions of concentration $1\,mol\,dm^{-3}$. Platinum is chosen because it is an inert metal, has very little tendency to be oxidised and does not react with acids. The reaction occurring in this half-cell is:

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

and this is arbitrarily assigned a standard electrode potential ($E^{\ominus}$) of 0.00 V.

Note: the reaction could also have been written as:

$$H^+(aq) + e^- \rightleftharpoons \tfrac{1}{2}H_2(g) \qquad\qquad E^{\ominus} = 0.00\,V$$
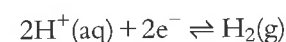
Figure 9.18 The standard hydrogen electrode. Note: $1\,M = 1\,mol\,dm^{-3}$.

Exam tip
$1\,mol\,dm^{-3}\ H_2SO_4(aq)$ is not suitable for use in the standard hydrogen electrode because $H_2SO_4(aq)$ is a diprotic acid and the concentration of $H+(aq)$ will be greater than $1\,mol\,dm^{-3}$.
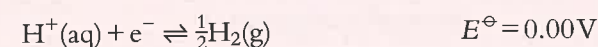
Measuring standard electrode potentials

The standard electrode potential ($E^{\ominus}$) of copper could be measured by connecting a standard copper half-cell ($1\,mol\,dm^{-3}\ Cu^{2+}(aq)/Cu(s)$) to the standard hydrogen electrode (Figure **9.19**).
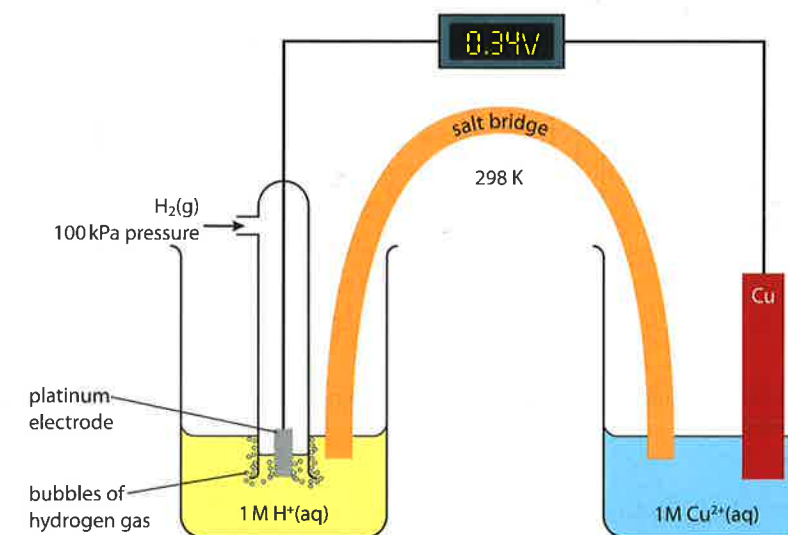
Figure 9.19 Measuring the standard electrode potential of the Cu^{2+}/Cu half-cell. Note: $1\,M = 1\,mol\,dm^{-3}$.

A voltmeter with very high resistance is used so that the current is as low as possible. If current flows, the concentrations of the species in the half-cells will change and the system will no longer be under standard conditions.

The reactions that occur in the half-cells are:

$$H_2(g) \rightarrow 2H^+(aq) + 2e^- \qquad\qquad Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

The hydrogen is oxidised and the copper(II) ions are reduced.

The cell potential when copper is attached to a standard hydrogen electrode is 0.34 V and we can write:

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

So the standard electrode potential of copper is +0.34 V. The half-equations for standard electrode potentials are always written as reduction reactions and, because the reduction of Cu^{2+} occurs when it is attached to a standard hydrogen electrode, the standard electrode potential has a positive sign, which indicates that the reduction of copper(II) ions is favourable compared with the standard hydrogen electrode.

Figure **9.20** shows a cell in which a standard zinc half-cell is connected to a standard hydrogen electrode. The reactions are:

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \qquad\qquad Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

The cell potential is 0.76 V. The zinc is oxidised when attached to the standard hydrogen electrode, but because a standard electrode potential is always written in terms of a reduction reaction, we write:

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

The negative sign indicates that it is the reverse reaction that is favourable when the zinc half-cell is connected to a standard hydrogen electrode.

The **standard electrode potential** is the EMF (voltage) of a half-cell connected to a standard hydrogen electrode, measured under standard conditions. All solutions must be of concentration $1 \, mol \, dm^{-3}$.

A standard electrode potential is always quoted for the reduction reaction.

Figure 9.20 Measuring the standard electrode potential of the Zn^{2+}/Zn half-cell. Note: $1 \, M = 1 \, mol \, dm^{-3}$.

Some standard electrode potentials are given in Table **9.7**.

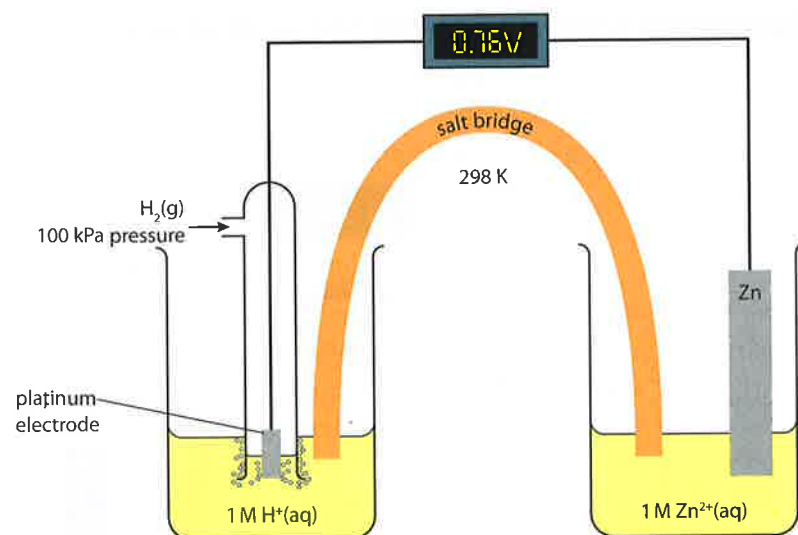| Half-equation	$E^{\ominus}/V$
$K^+(aq) + e^- \rightleftharpoons K(s)$	−2.92
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.36
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	−1.18
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.44
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	−0.23
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	−0.13
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.09
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$2BrO_3^-(aq) + 12H^+(aq) + 10e^- \rightleftharpoons Br_2(aq) + 6H_2O(l)$	+1.52
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87

Table 9.7 Some standard electrode potentials.

Note, in some tables of standard electrode potentials the half-equations for the F_2/F^- reaction, for example, are written as:

$$\tfrac{1}{2}F_2(g) + e^- \rightleftharpoons F^-(aq)$$
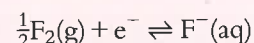
This makes absolutely no difference to the value of the standard electrode potential.

Working out cell potentials

We can use standard electrode potentials to work out the cell potential of the $Zn|Zn^{2+}||Ni^{2+}|Ni$ cell (Figure **9.21**).

The standard electrode potentials are:

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad E^{\ominus} = -0.76 \, V$$
$$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s) \qquad E^{\ominus} = -0.23 \, V$$

However, both of these are written as reduction reactions and in any cell there must be a reduction reaction *and* an oxidation reaction. One of the reactions must occur in the reverse direction.

Because the value of the standard electrode potential is more negative for the Zn^{2+}/Zn reaction, this means that the oxidation reaction is more favourable for zinc than for nickel. We therefore reverse the zinc half-equation:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad E^{\ominus} = +0.76 \, V \qquad \textbf{oxidation}$$
$$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s) \qquad E^{\ominus} = -0.23 \, V \qquad \textbf{reduction}$$
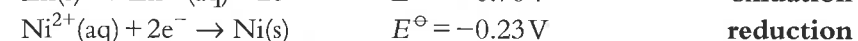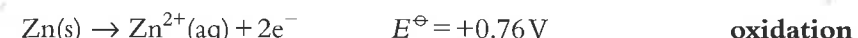
The cell potential is just the sum of these electrode potentials:

$$E^{\ominus}_{cell} = 0.76 - 0.23 = +0.53 \, V$$

An overall positive value indicates a spontaneous reaction.

The overall equation for the redox reaction is obtained by adding together the two half-equations (checking first that the numbers of electrons balance):

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad \textbf{oxidation}$$
$$\underline{Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)} \qquad \textbf{reduction}$$
$$Zn(s) + Ni^{2+}(aq) \rightarrow Zn^{2+}(aq) + Ni(s) \qquad \textbf{overall redox reaction}$$
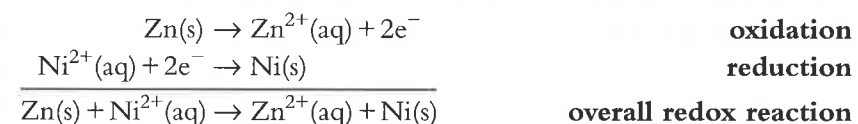
When a cell reaction is written using cell notation:

$$Zn|Zn^{2+}||Ni^{2+}|Ni$$
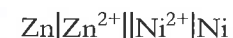
we can work out the cell potential using the equation:

$$E^{\ominus}_{cell} = E^{\ominus}_{rhs} - E^{\ominus}_{lhs}$$

where $E^{\ominus}_{rhs}$ is the standard electrode potential on the right-hand side of the cell notation and $E^{\ominus}_{lhs}$ is the standard electrode potential on the left-hand side of the cell notation.

In this case, $E^{\ominus}_{cell} = -0.23 - (-0.76) = +0.53 \, V$

Figure 9.21 A zinc–nickel cell.

In general, the procedure for calculating a cell potential is:
1 Write down the half-equations and standard electrode potentials for the two reactions involved.
2 Change the sign of the more negative (less positive) standard electrode potential and add it to the other electrode potential.

We are always looking for a cell potential that is positive overall, as a positive value indicates a spontaneous reaction.

Worked example

9.5 Work out the overall reaction and calculate the cell potential for a cell consisting of an Fe^{3+}/Fe^{2+} half-cell and a Zn^{2+}/Zn half-cell.

The two half-equations are:

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

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \qquad E^{\ominus} = +0.77\,V$$

The more negative value is $-0.76\,V$, and this half-equation is reversed:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \qquad E^{\ominus} = +0.76\,V \qquad \textbf{oxidation}$$
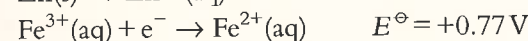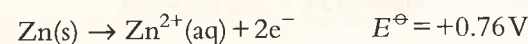
$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \qquad E^{\ominus} = +0.77\,V \qquad \textbf{reduction}$$

The electrode potential values are added together to give the cell potential:

$$E^{\ominus}_{cell} = 0.76 + 0.77 = +1.53\,V \qquad \boxed{\text{positive cell potential} = \text{spontaneous}}$$

In order to combine the two half-equations to produce the overall redox equation, the Fe^{3+}/Fe^{2+} half-equation must be multiplied by two so that the number of electrons is the same in the two half-equations.
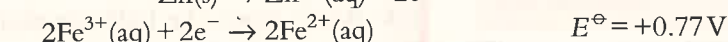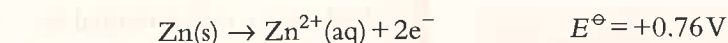
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$	$E^{\ominus} = +0.76\,V$	**oxidation**
$2Fe^{3+}(aq) + 2e^- \rightarrow 2Fe^{2+}(aq)$	$E^{\ominus} = +0.77\,V$	**reduction**
$Zn(s) + 2Fe^{3+}(aq) \rightarrow Zn^{2+}(aq) + 2Fe^{2+}(aq)$	$E^{\ominus}_{cell} = +1.53\,V$	**overall redox reaction**

> **Note:** although the Fe^{3+}/Fe^{2+} half-equation is multiplied by two, the standard electrode potential is not. A standard electrode potential indicates the potential for a reaction to occur – it is never multiplied by anything when working out a standard cell potential.

The polarity of the electrodes and the direction of electron flow in the external circuit

Consider again the cell made from $Mg|Mg^{2+}$ and $Zn^{2+}|Zn$ half-cells (Figure **9.22**). In the right-hand half-cell, the magnesium is oxidised and therefore electrons are lost. This means that the magnesium electrode is the negative one because electrons are released there. The electrons move through the ext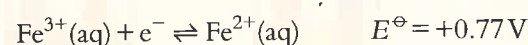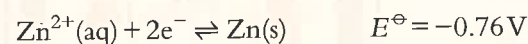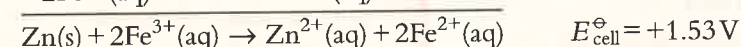ernal circuit from the magnesium to the zinc electrode, where they combine with Zn^{2+} ions in a reduction reaction. The zinc electrode is the positive electrode because electrons are used up there.

> The electrode at which oxidation occurs is the anode; therefore the magnesium electrode is the anode in Figure **9.22**. The electrode at which reduction occurs is the cathode; therefore the zinc electrode is the cathode.
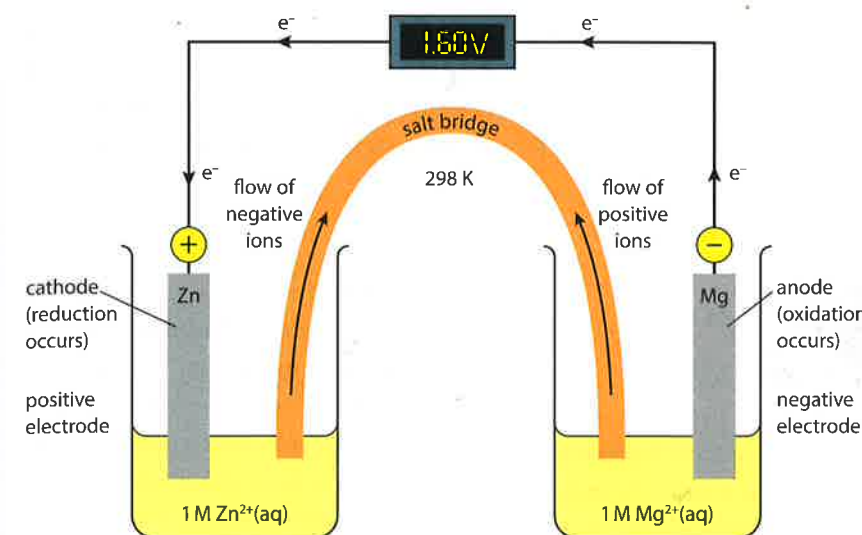
Figure 9.22 An $Mg|Mg^{2+}||Zn^{2+}|Zn$ cell.

Another way to determine which are the negative and positive electrodes is to just look at the original electrode potentials:

$$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s) \qquad E^{\ominus} = -2.36\,V$$

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

The electrode potential is more negative for the $Mg|Mg^{2+}$ half-cell – therefore the magnesium electrode is the negative electrode (and the zinc electrode is the positive electrode). The electrons flow from the negative electrode to the positive electrode – that is, from magnesium to zinc (Figure **9.22**). Negative charge always flows in the same continuous direction around the circuit, so negative ions will flow through the salt bridge from the zinc half-cell to the magnesium half-cell. Positive ions will flow in the opposite direction.

If the cell is written in terms of the cell notation, then the negative electrode is on the left and electrons flow through the external circuit from left to right (Figure **9.23**).

> **Note:** these are the original standard electrode potentials (for the reduction reactions) – neither has been reversed.

> **Exam tip**
> Whichever half-cell has the more negative standard electrode potential will be the negative electrode in the cell, and the electrons will flow from this half-cell to the other one.
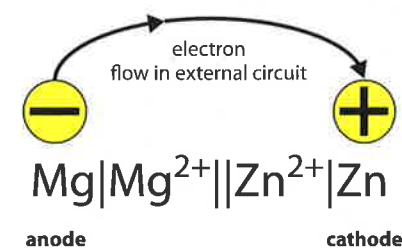
Figure 9.23 Cell notation is written so that the negative electrode is on the left.

Worked example

9.6 Predict the cell potential for a cell made up of $Cu|Cu^{2+}$ and $Ni|Ni^{2+}$ half-cells. Indicate which is the positive and which is the negative electrode. Give the direction of electron flow in the external circuit and write an overall equation for the reaction that occurs.

The half-equations and standard electrode potentials are:

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

$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $E^\ominus = -0.23\,V$
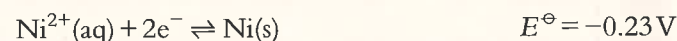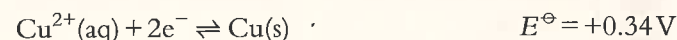
We can see immediately which is the negative and which the positive electrode. The Ni^{2+}/Ni standard electrode potential is more negative, and therefore this is the negative electrode. The electrons flow from the negative electrode (nickel) to the positive electrode (copper).

The more negative electrode potential is that for the Ni^{2+}/Ni reaction and so this half-equation is reversed:

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E^\ominus = +0.34\,V$ **reduction**

$Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$ $E^\ominus = +0.23\,V$ **oxidation**

$Cu^{2+}(aq) + Ni(s) \rightarrow Ni^{2+}(aq) + Cu(s)$ $E^\ominus_{cell} = +0.57\,V$ **overall redox reaction**

Electrons are lost at the nickel electrode, so this is this negative electrode. Electrons are gained at the copper electrode and so this is the positive electrode. Electrons flow from the nickel electrode to the copper electrode.

> **Exam tip**
> There is more than one half-equation in the data booklet involving copper – make sure that you select the correct one. You must always check that both the oxidised and reduced species are the same as in your half-equation.

> **Exam tip**
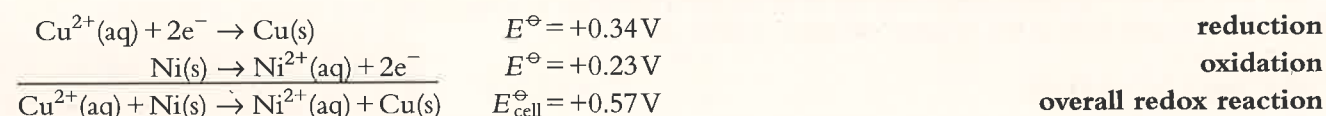> In the IB Chemistry data booklet, the electrode potentials are arranged from negative to positive. The half-equation higher up the table is therefore the one that is reversed to give the overall spontaneous reaction.

? Test yourself

18 Predict cell potentials for the following cells (use Table **9.7**, page **396**). Indicate which is the positive and which is the negative electrode. Give the direction of electron flow in the external circuit and write an overall equation for the reaction that occurs.
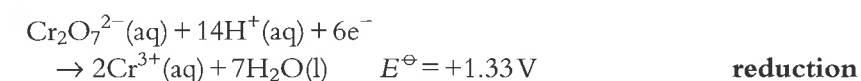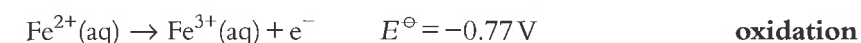
a $Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$

b $I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$ $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$

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

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

e $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$ $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$

f $Fe(s)|Fe^{2+}(aq)||Br_2(l)|Br^-(aq)|Pt$

Using standard electrode potentials to predict the feasibility of a redox reaction

In chemistry, rather than being concerned with generating electricity and voltaic cells, we usually use standard electrode potentials to predict whether or not a particular redox reaction is likely to occur. For instance, will acidified potassium dichromate(VI) oxidise iron(II) ions? If we examine the relevant half-equations we get:

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

$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ $E^\ominus = +0.77\,V$

We are looking at the possibility of Fe^{2+} being oxidised to Fe^{3+} and therefore we must reverse this half-equation:

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$ $E^\ominus = -0.77\,V$ **oxidation**

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ $E^\ominus = +1.33\,V$ **reduction**

When we add up these values we get $E^\ominus_{cell} = 1.33 - 0.77 = +0.56\,V$.

The positive value indicates that the reaction will be spontaneous, so Fe^{2+} ions will be oxidised to Fe^{3+} ions by acidified dichromate(VI) ions.

The overall redox equation is obtained by multiplying the oxidation half-equation by 6 (so that the electrons balance) and then adding it to the reduction half-equation:

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Fe^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 6Fe^{3+}(aq)$
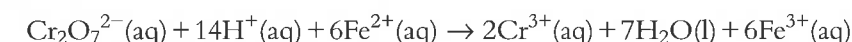
> As with using ΔG to predict the spontaneity of a reaction, the fact that a reaction is spontaneous does not tell us anything about the speed of the reaction. Although this reaction occurs relatively rapidly at room temperature, this will not always be the case and some reaction mixtures will need heating to occur at a significant rate.

> Predictions using standard electrode potentials are valid only under standard conditions – that is, at $298\,K$ and $100\,kPa$ with $1\,mol\,dm^{-3}$ solutions. However, so long as the values are not too close to zero, the predictions are likely to be useful even when a reaction is carried out under non-standard conditions.

Worked example

9.7 Predict, using standard electrode potentials, whether or not acidified potassium dichromate(VI) will oxidise Cl^- ions to Cl_2.

The half-equations are:

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$ $E^\ominus = +1.33\,V$
$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E^\ominus = +1.36\,V$
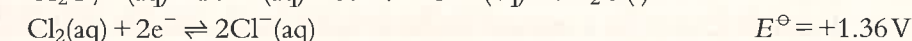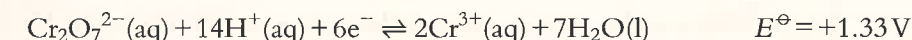
We are looking at the possibility of Cl^- ions being oxidised and must therefore reverse this half-equation:

$2Cl^-(aq) \rightarrow Cl_2(aq) + 2e^-$ $E^\ominus = -1.36\,V$ **oxidation**
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ $E^\ominus = +1.33\,V$ **reduction**
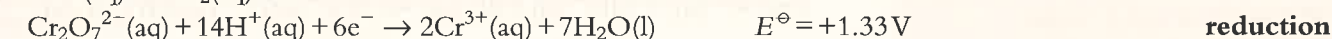
When the electrode potentials are added together we get $E^\ominus_{cell} = 1.33 - 1.36 = -0.03\,V$. The value is negative, which indicates that the reaction will not be spontaneous under standard conditions, and acidified dichromate(VI) will not oxidise Cl^- to Cl_2.

Oxidising and reducing agents

A very positive value for $E^{\ominus}$, for example:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) \qquad E^{\ominus} = +1.33\,V$$
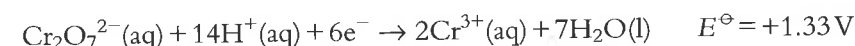
means that the reduction reaction is very favourable (relative to the standard hydrogen electrode), and the substance has a very strong tendency to pick up electrons from other species – i.e. it is a strong oxidising agent.

> **Oxidising agents have a strong tendency to remove electrons from other things substances – i.e. oxidise other species. Oxidising agents are substances that are readily reduced.**

A very negative value of the standard electrode potential, for example:

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

indicates that the reverse reaction is very favourable:

$$Na(s) \rightarrow Na^+(aq) + e^- \qquad E^{\ominus} = +2.71\,V$$
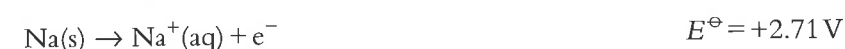
So, sodium has a very strong tendency to give electrons to other species – that is, to reduce other species. So, Na is a very good reducing agent.

In general we can say:

> **a substance with a more positive standard electrode potential will oxidise a substance with a less positive electrode potential**
> **or**
> **a substance with a more negative standard electrode potential will reduce a substance with a less negative standard electrode potential.**

Example 1

Consider the half-equations:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l) \qquad E^{\ominus} = +1.33\,V$$

$$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq) \qquad E^{\ominus} = +0.54\,V$$

$Cr_2O_7^{2-}$ has a more positive standard electrode potential than I_2, and therefore $Cr_2O_7^{2-}$ is a stronger oxidising agent than I_2 and will oxidise I^- to I_2.

The overall reaction is:

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^-(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3I_2(aq)$$

$$E^{\ominus}_{cell} = 1.33 - 0.54 = +0.79\,V$$

The more positive the standard electrode potential, the stronger the oxidising agent.

The more negative the standard electrode potential, the stronger the reducing agent.
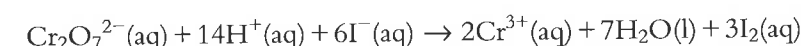
In this reaction, $Cr_2O_7^{2-}$ is the oxidising agent and I^- is the reducing agent.

Example 2

Consider the half-equations:

$$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s) \qquad E^{\ominus} = -2.36\,V$$

$$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s) \qquad E^{\ominus} = -0.13\,V$$

The standard electrode potential of the $Mg^{2+}|Mg$ half-cell is more negative than that of the $Pb^{2+}|Pb$ half-cell, which indicates that Mg is a stronger reducing agent than Pb and that Mg will therefore reduce Pb^{2+} to Pb.

The overall equation is:

$$Mg(s) + Pb^{2+}(aq) \rightarrow Mg^{2+}(aq) + Pb(s) \qquad E^{\ominus}_{cell} = +2.23\,V$$

In this reaction, Mg is the reducing agent and Pb^{2+} is the oxidising agent.
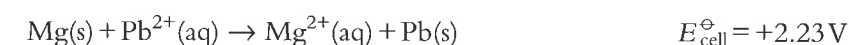
Let us consider the standard electrode potentials in Table **9.8**. Species on the right of the reversible arrow higher in the table reduce t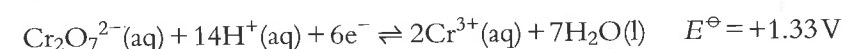hose on the left of the reversible arrow lower in the table. So, Na will reduce Mg^{2+} ions, and Zn will reduce Fe^{2+} ions. Species on the left of the reversible arrow lower in the table oxidise those on the right of the reversible arrow higher in the table – BrO_3^- will oxidise Cl^- and Br_2 will oxidise I^-.

Half-equation	$E^{\ominus}/V$
$K^+(aq) + e^- \rightleftharpoons K(s)$	−2.92
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.36
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.44
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	−0.23
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	−0.13
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.09
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$2BrO_3^-(aq) + 12H^+(aq) + 10e^- \rightleftharpoons Br_2(aq) + 6H_2O(l)$	+1.52
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87

Table 9.8 The connection between standard electrode potentials and oxidising/reducing ability.

strongest reducing agent (K)

decreasing strength of reducing agent

decreasing strength of oxidising agent
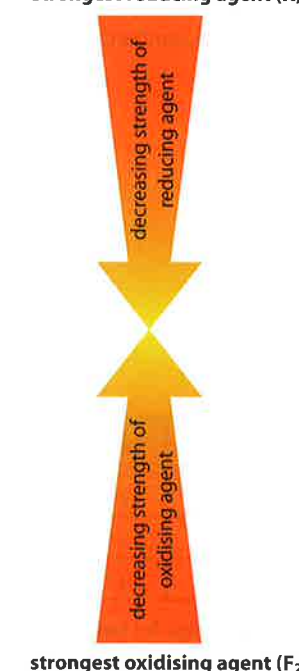
strongest oxidising agent (F_2)

The activity series and electrode potentials – the electrochemical series

We saw earlier in this topic that a more reactive metal will displace a less reactive metal from solution. For example, zinc is more reactive than copper and displaces copper(II) ions from solution:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \qquad E^{\ominus}_{cell} = +1.10\,V$$
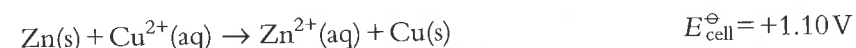
In terms of standard electrode potentials, the more reactive a metal, the more negative its standard electrode potential. The more negative standard electrode potential indicates that the reduction reaction of the metal ion is very unfavourable and therefore that the oxidation of the metal is very favourable. More reactive metals have a greater tendency to be oxidised and thus give electrons to (reduce) other species.

In Table **9.9**, Mg is the most reactive metal and Ag the least reactive.

Metals above hydrogen in the activity series are stronger reducing agents than hydrogen and should displace hydrogen from a solution of its ions – that is, from acids:

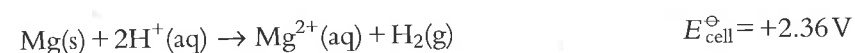$$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g) \qquad E^{\ominus}_{cell} = +2.36\,V$$
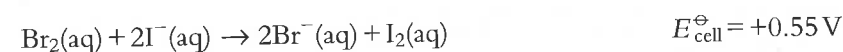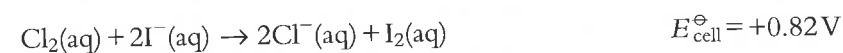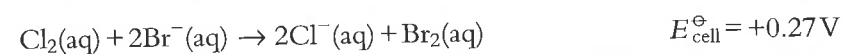
Metals lower than hydrogen in the activity series will not react with acids – so copper and silver do not react with hydrochloric acid.

In terms of standard electrode potentials, any metal with a negative standard electrode potential is a stronger reducing agent than hydrogen ($E^{\ominus} = 0.00\,V$) and reduces hydrogen ions to hydrogen gas. In other words, metals with negative standard electrode potentials should liberate hydrogen from acids.

We can consider the reactivity of the halogens in terms of their oxidising ability. Chlorine is a stronger oxidising agent than bromine and iodine and will oxidise bromide ions to bromine and iodide ions to iodine. Bromine is a stronger oxidising agent than iodine and will oxidise iodide ions to iodine. In terms of electrons, chlorine has the strongest affinity for electrons and will remove electrons from bromide ions and iodide ions.

Let us consider the standard electrode potentials in Table **9.10**. Chlorine has the most positive standard electrode potential and is therefore the strongest oxidising agent:

$$Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq) \qquad E^{\ominus}_{cell} = +0.27\,V$$

$$Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq) \qquad E^{\ominus}_{cell} = +0.82\,V$$

$$Br_2(aq) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(aq) \qquad E^{\ominus}_{cell} = +0.55\,V$$

All these reactions have a positive cell potential and are, therefore, all spontaneous. All other possible reactions between the halogens and the halide ions would have a negative electrode potential and are therefore not spontaneous, for example:

$$Br_2(aq) + 2Cl^-(aq) \rightarrow 2Br^-(aq) + Cl_2(aq) \qquad E^{\ominus}_{cell} = -0.27\,V$$
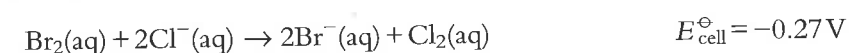
	$E^{\ominus}/V$
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.36
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.44
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	−0.23
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(aq)$	+0.34
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80

Table 9.9 Activity series and standard electrode potentials.

	$E^{\ominus}/V$
$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.09
$Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36

Table 9.10 Standard potentials for halogens.

Test yourself

19 Use standard electrode potentials to predict whether the following reactions will be spontaneous. If the reaction is spontaneous, state the oxidising agent and the reducing agent.
 a $Cu(s) + Mg^{2+}(aq) \rightarrow Cu^{2+}(aq) + Mg(s)$
 b $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Br^-(aq)$
    $\rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3Br_2(l)$
 c $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6F^-(aq)$
    $\rightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3F_2(g)$
 d $5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$
    $\rightarrow 5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq)$

20 Consider the following standard electrode potentials:

$U^{4+} + e^- \rightleftharpoons U^{3+}$	$E^{\ominus} = -0.61\,V$
$U^{3+} + 3e^- \rightleftharpoons U$	$E^{\ominus} = -1.79\,V$
$Eu^{3+} + e^- \rightleftharpoons Eu^{2+}$	$E^{\ominus} = -0.43\,V$
$Po^{2+} + 2e^- \rightleftharpoons Po$	$E^{\ominus} = +0.65\,V$
$In^{3+} + 3e^- \rightleftharpoons In$	$E^{\ominus} = -0.34\,V$
$Sm^{3+} + e^- \rightleftharpoons Sm^{2+}$	$E^{\ominus} = -1.15\,V$
$Np^{3+} + 3e^- \rightleftharpoons Np$	$E^{\ominus} = -1.86\,V$
$Np^{4+} + e^- \rightleftharpoons Np^{3+}$	$E^{\ominus} = +0.15\,V$
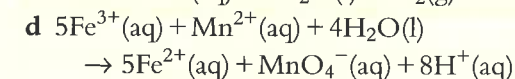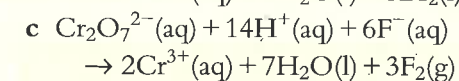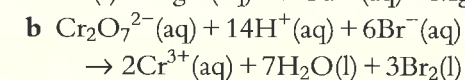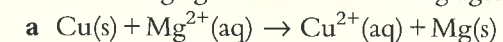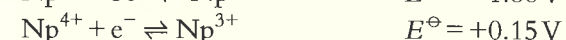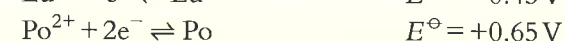
 a Select from this list:
    i the strongest oxidising agent
    ii the strongest reducing agent
 b Use the standard electrode potentials above to work out whether the following statements are **true** or **false**:
    i Eu^{2+} will reduce In^{3+} to In
    ii Sm^{3+} will oxidise Np to Np^{3+}
    iii Po will reduce Sm^{3+} to Sm^{2+}
    iv Np^{3+} is a stronger reducing agent than Po
    v U is a stronger reducing agent than Np
    vi Np^{3+} will reduce Po^{2+} to Po but will not oxidise Eu^{2+} to Eu^{3+}
    vii Sm^{2+} will not reduce U^{3+} to U but will reduce U^{4+} to U^{3+}
 c Predict whether or not the following reactions will be spontaneous:
    i $3Eu^{3+} + In \rightarrow 3Eu^{2+} + In^{3+}$
    ii $2Eu^{2+} + Po^{2+} \rightarrow 2Eu^{3+} + Po$
    iii $3Np^{3+} + In \rightarrow 3Np^{4+} + In^{3+}$

Standard cell potentials and $\Delta G^{\ominus}$

The standard cell potential and the standard free energy change ($\Delta G^{\ominus}$) are related by the equation:

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

where n is the number of electrons transferred in a particular redox reaction and F is the Faraday constant, which is equal to the charge on one mole of electrons and has a value of approximately $96\,500\,C\,mol^{-1}$.

Example
Calculate $\Delta G^{\ominus}$ for the reaction:

$$Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$$
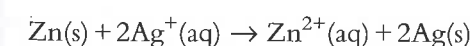
The cell potential can be worked out from the standard electrode potentials ($Zn^{2+}/Zn = -0.76\,V$ and $Ag^+/Ag = +0.80\,V$):

$$E^{\ominus}_{cell} = 0.76 + 0.80 = 1.56\,V$$

If the overall equation is split into its two half-equations:

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

$$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$$
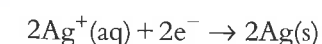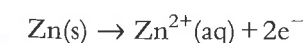
It can be seen that two electrons are transferred from the zinc to the silver ions, therefore $n = 2$.

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

$$\Delta G^{\ominus} = -2 \times 96\,500 \times 1.56 = -301\,000\,J\,mol^{-1}$$

We normally quote $\Delta G^{\ominus}$ values in $kJ\,mol^{-1}$, therefore

$$\Delta G^{\ominus} = -301\,kJ\,mol^{-1}$$

So, both $E^{\ominus}_{cell}$ and $\Delta G^{\ominus}$ can be used to predict whether a reaction is spontaneous or not (Table **9.11**).

$E^{\ominus}_{cell}$	$\Delta G^{\ominus}$	Spontaneous?
positive	negative	spontaneous
negative	positive	non-spontaneous
0	0	at equilibrium

Table 9.11 The relationship between $E^{\ominus}_{cell}$, $\Delta G^{\ominus}$ and spontaneity.

? Test yourself

21 Work out the cell potential and $\Delta G^{\ominus}$ for each of the following and predict whether the reaction will be spontaneous or not:

a $Zn(s) + Ni^{2+}(aq) \rightarrow Zn^{2+}(aq) + Ni(s)$
b $Pb^{2+}(aq) + Cu(s) \rightarrow Pb(s) + Cu^{2+}(aq)$
c $Cr_2O_7^{2-}(aq) + 6I^-(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3I_2(aq) + 7H_2O(l)$

9.3.2 Electrolysis of aqueous solutions

Ionic salts conduct electricity when dissolved in water because the ions are free to move. These solutions can be electrolysed, but the products are not as straightforward as in electrolysis of molten salts. The general rule for the products formed at the electrodes when aqueous solutions are electrolysed is shown in Table **9.12**.

Electrode	Product
positive (**anode**)	oxygen or a halogen
negative (**cathode**)	a metal or hydrogen

Table 9.12 Products at the electrodes when aqueous solutions are electrolysed.

The products obtained from the electrolysis of various $1\,mol\,dm^{-3}$ solutions using platinum electrodes are given in Table **9.13**.

Solution	Product at anode (+)	Product at cathode (−)
copper(II) chloride	chlorine gas	copper metal
copper(II) sulfate	oxygen gas	copper metal
sodium chloride	chlorine gas	hydrogen gas
hydrochloric acid	chlorine gas	hydrogen gas
water (acidified)	oxygen gas	hydrogen gas

Table 9.13 Electrolysis products of aqueous solutions using platinum electrodes.

There are three main factors that influence the products formed when an aqueous solution of a salt is electrolysed:

- the standard electrode potentials of the species in solution
- the concentration of the electrolyte
- the material from which the electrodes are made.

Using standard electrode potentials to predict the product of electrolysis
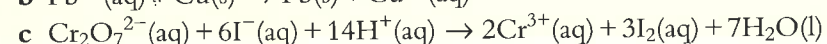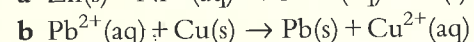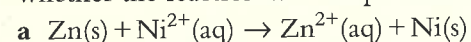
We will first of all look at the products at the cathode. When sodium chloride solution is electrolysed, a reduction reaction occurs at the cathode and hydrogen gas is formed. The two possible species that are present in the solution that could be reduced are Na^+ and H_2O. Let us consider the standard electrode potentials for the reduction of Na^+ and water:

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

$$H_2O(l) + e^- \rightleftharpoons \tfrac{1}{2}H_2(g) + OH^-(aq) \qquad\qquad E^{\ominus} = -0.83\,V$$

It can be seen that the standard electrode potential for the reduction of water is much more positive than that for the reduction of Na^+. Therefore the reduction of water is more favourable than the reduction of Na^+, and hydrogen will be formed from the reduction of water rather than sodium metal from the reduction of Na^+.

If we then compare this with the electrolysis of copper(II) sulfate solution, the electrode potentials for the possible reduction reactions are:

$$H_2O(l) + e^- \rightleftharpoons \tfrac{1}{2}H_2(g) + OH^-(aq) \qquad\qquad E^{\ominus} = -0.83\,V$$

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

It can be seen that it is more favourable to reduce Cu^{2+} ions than to reduce water and therefore copper, from the reduction of Cu^{2+}, will be formed at the cathode rather than hydrogen.

In general, metals can be divided into three groups.

1 Very reactive metals (with very negative standard electrode potentials), such as sodium, potassium and magnesium – that is, metals above zinc in the activity series. These produce hydrogen when aqueous solutions of their ions are electrolysed.

2 Unreactive metals (with positive standard electrode potentials), such as copper and silver. These produce the metal when aqueous solutions of their ions are electrolysed.

3 Metals of intermediate reactivity (with standard electrode potentials between -0.83 V and 0.00 V), such as zinc, nickel and lead. For these metals it is much more difficult to make predictions and we can get either the metal or a mixture of the metal and hydrogen, depending on the metal and the conditions used.

We can see that it is possible, to a certain extent, to predict the products of electrolysis of aqueous solutions based on the reactivity of the metals and their standard electrode potentials. Problems with using standard electrode potentials arise because they refer to standard conditions (1 mol dm^{-3} concentrations) and to solutions containing both the oxidised and the reduced species.

Formation of halogens during electrolysis of aqueous solutions

When a solution of sodium iodide is electrolysed, iodine is produced at the anode but when a solution of sodium fluoride is electrolysed, oxygen (from the oxidation of water) is produced at the anode. This can be explained in term of how easy it is to oxidise the halide ions to the element, compared to the oxidation of water – standard electrode potentials can be used as a guide to this.

Consider these standard electrode potentials:

$$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq) \qquad\qquad E^\ominus = +0.54\,\text{V}$$
$$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l) \qquad E^\ominus = +1.23\,\text{V}$$
$$F_2(s) + 2e^- \rightleftharpoons 2F^-(aq) \qquad\qquad E^\ominus = +2.87\,\text{V}$$

At the anode, oxidation occurs and therefore we can reverse all these half-equations to get the oxidation reaction:

$$2I^-(aq) \rightarrow I_2(s) + 2e^- \qquad\qquad E_{ox} = -0.54\,\text{V}$$
$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad E_{ox} = -1.23\,\text{V}$$
$$2F^-(aq) \rightarrow F_2(g) + 2e^- \qquad\qquad E_{ox} = -2.87\,\text{V}$$

At the anode, two oxidation reactions are possible – either the halide ion can be oxidised to produce the halogen, or water can be oxidised to produce oxygen. From these values it can be seen that it is more favourable to oxidise I^- ions (more positive potential for oxidation) than to oxidise water, but it is less favourable to oxidise F^- ions (more negative potential for oxidation). So in NaI(aq), iodide ions will be oxidised at the anode to produce iodine, but in NaF(aq), water will be oxidised in preference to fluoride ions to produce oxygen gas at the anode.

The anode product in the electrolysis of copper(II) sulfate using graphite electrodes

Oxygen is produced at the anode from the oxidation of water:

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad \textbf{oxidation}$$

Sulfates contain sulfur in its highest oxidation state and therefore it is not susceptible to oxidation.

It is actually possible to oxidise the SO_4^{2-} ion, but this is much more difficult than the oxidation of water:

$$2H_2O(l) \rightleftharpoons O_2(g) + 4H^+(aq) + 4e^- \qquad E_{ox} = -1.23\,\text{V}$$
$$SO_4^{2-}(aq) \rightleftharpoons \tfrac{1}{2}S_2O_8^{2-}(aq) + e^- \qquad E_{ox} = -2.01\,\text{V}$$

$S_2O_8^{2-}$ contains a peroxo group, so the oxidation state of S is still $+6$; the O is oxidised.

The effect of concentration of the electrolyte on the products at the electrodes

We will consider the products at the anode when a solution of sodium chloride is electrolysed. The two species in solution that can be oxidised at the anode are Cl^- and H_2O and the equations with the relevant standard electrode potentials are:

$$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l) \qquad E^\ominus = +1.23\,\text{V}$$
$$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq) \qquad E^\ominus = +1.36\,\text{V}$$

We are, however, interested in the oxidation reactions and these equations must be reversed:

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad E_{ox} = -1.23\,\text{V}$$
$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^- \qquad E_{ox} = -1.36\,\text{V}$$

From these values it can be seen that it is slightly more favourable (E_{ox} more positive) to oxidise H_2O to form oxygen than to oxidise Cl^- to form chlorine. If a solution of sodium chloride of low concentration is electrolysed, the major product at the anode is oxygen. However, these values are very close together and at higher concentrations of sodium chloride, chlorine becomes the major product.

The nature of the electrodes affects the products formed

In order to illustrate this, we will consider the electrolysis of copper sulfate solution using two different sets of electrodes. Different products are obtained at the anode depending on the material of which the electrodes are made.

Electrolysis of copper(II) sulfate solution using inert electrodes (graphite or platinum)

The electrolysis of copper sulfate solution using platinum electrodes is shown in Figure 9.24. The products and half-equations at each electrode are shown in Table 9.14.
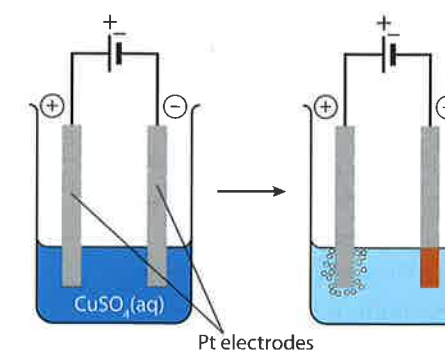
Figure 9.24 Electrolysis of copper sulfate solution using platinum electrodes.

Electrode	Product	Half-equation
anode (+)	oxygen	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
cathode (−)	copper	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Table 9.14 Electrolysis of copper(II) sulfate solution with platinum electrodes.

During the experiment, the cathode (−) becomes coated in a brown metal (copper), bubbles of a colourless gas (oxygen) are given off at the anode (+), the blue colour of the solution fades and the solution becomes more acidic (test with a pH meter or pH paper).

The blue colour of the solution is due to the presence of $Cu^{2+}(aq)$ ions. The colour of the solution becomes paler as the Cu^{2+} ions are removed from the solution by reduction at the cathode.

The oxidation of water at the anode produces H^+ ions as well as O_2. This means that the solution becomes acidic.

The sulfate ions remain unchanged in the solution, and, because H^+ ions are also produced, the remaining solution after all the copper ions have been removed is sulfuric acid (H_2SO_4).

Electrolysis of copper(II) sulfate solution using copper electrodes

Electrolysis of copper sulfate solution using copper electrodes is shown in Figure **9.25**.

The positive electrode (anode) becomes smaller, the negative electrode (cathode) becomes coated with a brown metal (copper) and the solution remains the same colour.

The reaction at the cathode is exactly the same as when inert electrodes are used. However, at the anode the reaction is different and no oxygen is given off. The reaction at the anode is oxidation and two reactions are possible:

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^- \qquad E_{ox} = -0.34\,V$$

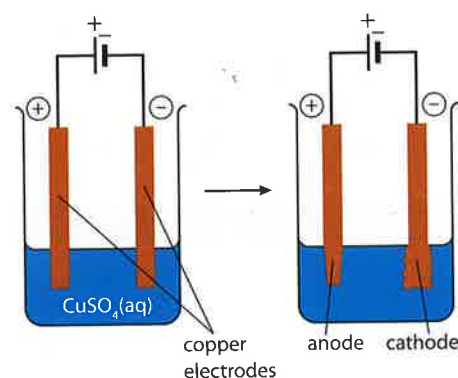$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad E_{ox} = -1.23\,V$$

The potential for oxidation of copper is more positive than that for the oxidation of water, and therefore the oxidation of copper is more favourable than the oxidation of water. So copper ions pass into solution from the anode and oxygen is not produced. The oxidation of copper at the anode was not possible when inert electrodes were used.

The overall processes that occur are summarised in Table **9.15**.

Figure 9.25 Electrolysis of copper sulfate solution using copper electrodes.

This process is used in the purification of copper. The anode is made of impure copper and the cathode of pure copper. Copper dissolves from the anode and is deposited as pure copper at the cathode. Impurities are either left as a sludge below the anode or go into solution. The gain in mass of the cathode is less than the loss in mass of the anode as a result of the impurities.

Electrode	Product	Half-equation
anode (+)	copper ions pass into solution	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
cathode (−)	copper	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Table 9.15 Electrolysis of copper(II) sulfate solution with copper electrodes.

The net process is therefore a transfer of copper from the anode to the cathode. If pure copper electrodes are used, the mass of copper lost from the anode is equal to the mass of copper deposited on the cathode.

Because one Cu^{2+} ion is removed from the solution at the cathode for every Cu^{2+} ion added to the solution at the anode, the overall concentration of Cu^{2+} ions in the electrolyte does not change and the blue colour of the solution remains constant.

Electroplating

Electroplating is the process of coating an object with a thin layer of a metal using electrolysis. The object to be coated should be used as the cathode, the anode should be made of the metal with which the object is to be plated and the electrolyte will normally be a solution containing the ions of the coating metal. The object to be plated must be the cathode (−) because metal ions are positively charged and will be attracted to the cathode. The object to be plated must be thoroughly cleaned before electroplating, otherwise the coating will not stick properly to the surface. Figure **9.26** shows the experimental set-up for coating a key with copper.

The reactions involved are:

Electrode	Half-equation
anode (+)	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
cathode (−)	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

The processes here are essentially the same as for the electrolysis of copper sulfate solution using copper electrodes. The copper anode gets smaller as copper ions go into solution and the colour of the electrolyte remains constant as the concentration of $Cu^{2+}(aq)$ ions remains constant.

Steel objects can be electroplated with chromium to prevent rusting and to provide a decorative finish.
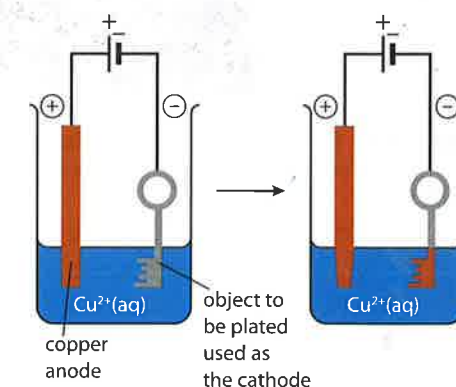
Figure 9.26 Experimental set-up for electroplating a key with copper.

Exam tip

The electrolyte must be a solution containing ions of the plating metal. To select a suitable solution, remember that all nitrates are soluble in water.
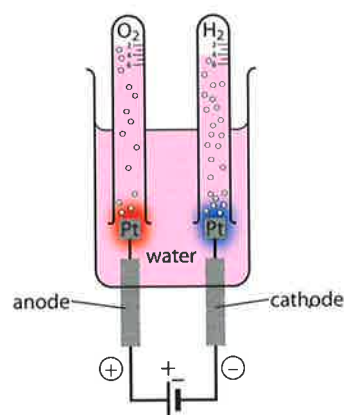
Electrolysis of water

Distilled water is a very poor conductor of electricity, and so the electrolysis of water is usually carried out on water to which small amount of sulfuric acid has been added ('acidified water'). Universal indicator has also been added to the water in Figure **9.27**.

The reaction that occurs at the anode (+) is oxidation of water:

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$$
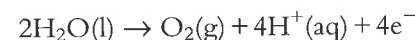
The product at the anode is oxygen gas. H^+ ions are also produced in this reaction and the universal indicator goes redder around the anode.

The reaction that occurs at the cathode (−) is reduction of water:

$$H_2O(l) + e^- \rightarrow \tfrac{1}{2}H_2(g) + OH^-(aq)$$
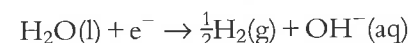
The product at the cathode is hydrogen gas. OH^- ions are also produced at the cathode, and the universal indicator goes blue around the cathode.

The H^+ ions produced at the anode combine with the OH^- ions formed at the cathode, so that the overall reaction when water is electrolysed is:

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

It can be seen from this equation that twice as much hydrogen as oxygen should be collected. Why this occurs can be understood by looking at the half-equations:

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + \mathbf{4e^-} \qquad \textbf{anode}$$
$$4H_2O(l) + \mathbf{4e^-} \rightarrow 2H_2(g) + 4OH^-(aq) \qquad \textbf{cathode}$$

When four electrons are lost at the anode, one molecule of O_2 is formed, but when four electrons are gained at the cathode, two molecu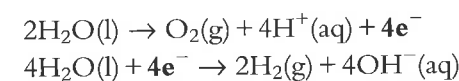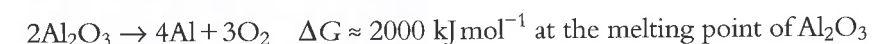les of H_2 are formed. Electrons must be lost from the anode at the same rate at which they are gained at the cathode (continuous flow of electrons in the external circuit), so two molecules of H_2 are formed for every molecule of O_2 formed.

Electrolysis and $\Delta G^{\ominus}$

The overall equation for the electrolysis of aluminium oxide is:

$$2Al_2O_3 \rightarrow 4Al + 3O_2 \quad \Delta G \approx 2000 \text{ kJ mol}^{-1} \text{ at the melting point of } Al_2O_3$$

The value of ΔG at the melting point of Al_2O_3 is very positive, indicating that the reaction is definitely not spontaneous at this temperature. However, passing of a current continually through the molten salt causes the non-spontaneous reaction to occur.

> The reaction that occurs in an electrolytic cell is non-spontaneous – electricity has to be supplied to cause it to occur (ΔG for the process is positive). This can be contrasted with a voltaic cell, in which a spontaneous reaction can be used to generate electricity (ΔG negative).

Figure 9.27 Electrolysis of acidified water to which some universal indicator has been added.

The half-equations have been written here so that the number of electrons is the same in each.

Quantitative electrolysis

In this section we will discuss the factors that affect the amounts of products formed at the electrodes.

The factors that affect the amount of product formed at an electrode are:
- the current
- the length of time of electrolysis
- the charge on the ion.

Current

The current that flows is directly proportional to the charge and hence to the number of electrons that flow around the circuit. This can be represented by the equation:

$$Q = It$$

where Q is the charge (in coulombs, C), I is the current (in amperes, A) and t is the time (in seconds, s).

If twice the current flows in a certain time, then twice as much charge will pass and twice as many electrons will be transferred to/from ions – therefore twice as many moles of substance will be produced.

Let us consider the half-equation:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$
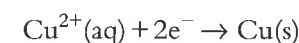
To produce one mole of copper, two moles of electrons must flow around the circuit. A current of about 2.23 A must flow for 24 hours to produce 1 mol copper. If a current of 4.46 A flows for 24 hours, twice as many electrons (4 mol) will flow around the circuit, and 2 mol copper will be formed.

Time of electrolysis

If current flows for twice the time, then twice as many electrons will be transferred and twice as much product will be formed.

Time, like current, is directly proportional to the charge, and hence the number of electrons, that flows around the circuit.

Charge on the ion

Consider the electrolysis of molten samples containing Na^+, Mg^{2+} and Al^{3+} ions. These ions will be reduced according to the equations:

$$Na^+ + e^- \rightarrow Na$$
$$Mg^{2+} + 2e^- \rightarrow Mg$$
$$Al^{3+} + 3e^- \rightarrow Al$$
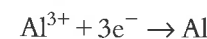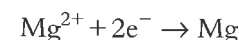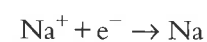
Therefore if three moles of electrons are passed through each electrolyte, 3 mol Na, 1.5 mol Mg and 1 mol Al will be obtained. This can also be seen if we rewrite the above half-equations using $3e^-$ in each:

$$3Na^+ + 3e^- \rightarrow 3Na$$
$$\tfrac{3}{2}Mg^{2+} + 3e^- \rightarrow \tfrac{3}{2}Mg$$
$$Al^{3+} + 3e^- \rightarrow Al$$
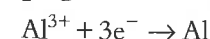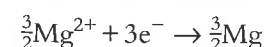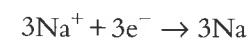
> The number of moles of substance produced at the electrodes is proportional to the current and the time and inversely proportional to the charge on the ion.

Worked examples

9.8 A solution of copper(II) sulfate is electrolysed using platinum electrodes. If 0.636 g of copper is produced at the cathode, calculate the volume of oxygen (measured at standard temperature and pressure) produced at the anode.

0.636 g of copper is $\dfrac{0.636}{63.55} = 0.0100\,\text{mol}$

The half-equation for the production of copper at the cathode is:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$
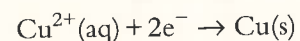
So two moles of electrons are required to produce one mole of copper. This means that the passage of 0.0200 mol electrons is required to produce 0.0100 mol copper.

The half-equation for the reaction at the anode is:

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$$
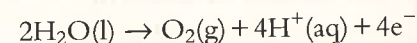
So four moles of electrons are required to produce one mole of O_2.
The number of moles of oxygen produced when 0.0200 mol electrons are passed is $\dfrac{0.0200}{4}$, or $5.00 \times 10^{-3}\,\text{mol}$.

The volume of oxygen produced at standard temperature and pressure is given by:

number of moles × molar volume

volume = $5.00 \times 10^{-3} \times 22.7 = 0.114\,\text{dm}^3$

> This is essentially the same approach as we used to work out moles problems in Topic **1**.

9.9 Two electrolytic cells are connected in series as shown in the diagram below. The first contains $1\,\text{mol}\,\text{dm}^{-3}$ sodium chloride solution and the second $1\,\text{mol}\,\text{dm}^{-3}$ copper(II) sulfate solution. Platinum electrodes are used throughout. Compare the volumes of each of the gases produced and the volumes of gas produced in each cell.
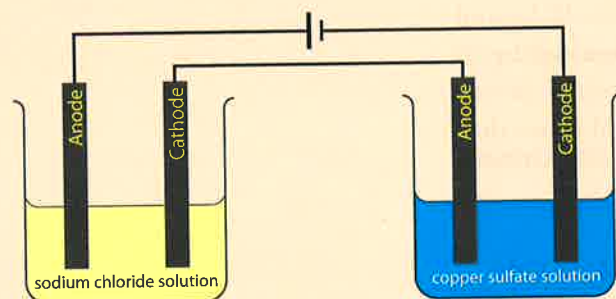
> Note that the anode in the copper sulfate cell is positive relative to the cathode in the same cell, but negatively charged relative to the cathode in the sodium chloride cell. Electrons flow from the anode of the copper sulfate cell to the cathode of the sodium chloride cell through the external circuit.

The products formed at the electrodes and the half-equations for their formation are as follows:

NaCl(aq)

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

CuSO₄(aq)
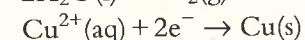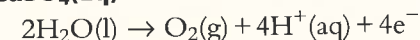
$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$	anode
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	cathode

Because the cells are connected in series the same current passes through each cell.

If we rewrite the equations involving gases so that the same number of electrons is transferred in each we get:

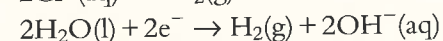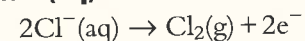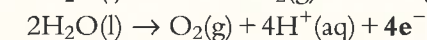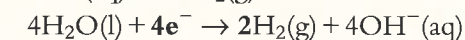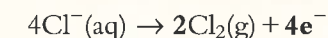|	
$4Cl^-(aq) \rightarrow 2Cl_2(g) + 4e^-$	**chlorine**
$4H_2O(l) + 4e^- \rightarrow 2H_2(g) + 4OH^-(aq)$	**hydrogen**
$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$	**oxygen**

From this it can be seen that the volumes of chlorine and hydrogen produced would be the same, but the volume of oxygen produced would be half that of either of the other two gases. Therefore, for every mole of oxygen gas produced, two moles of hydrogen and two moles of chlorine are produced.

The total volume of gas produced in the first cell (chlorine and hydrogen) is thus four times the amount of gas produced in the second cell (oxygen).

> Actually, if the experiment is carried out in the laboratory, the results will not match this exactly, as the gases are soluble to different extents in water.

Nature of science

Scientists can use quantitative data to test theories and models but must be aware of possible sources of errors in experimental method. For example, when measuring the volumes of different gases collected during electrolysis they must take account of the gases having different solubilities in water. When looking at the decrease in mass of, say, a copper electrode they must be aware that the electrode may not have been pure copper to start with.

Hydrogen fuels cells are being increasingly used to power vehicles and are being promoted as an environmentally friendly alternative to petrol and diesel-powered vehicles. This technology is a major area of research but there are many factors to consider when deciding how environmentally friendly fuel cells are. For instance, the production of the materials used to construct the fuel cells and how the hydrogen is generated are major considerations.

> Hydrogen fuels cells and microbial fuels cells, which are another area of research with environmental implications, are discussed in Option C.

? Test yourself

22 Predict the products at the anode and cathode when the following aqueous solutions are electrolysed using platinum electrodes:
  a potassium iodide solution
  b calcium nitrate solution
  c concentrated potassium chloride solution
  d magnesium sulfate solution
  e silver nitrate solution

23 Write equations for the reactions at the anode and cathode when the following solutions are electrolysed using platinum electrodes:
  a sodium sulfate solution
  b silver fluoride solution
  c magnesium nitrate solution

24 0.20 mol electrons are passed through each of the following electrolytic cells. In each case state the number of moles of each product formed.
  a molten sodium chloride
  b aqueous (concentrated) copper chloride solution
  c aqueous potassium sulfate solution

Exam-style questions

1 Which compound contains chlorine with the lowest oxidation number?

    A $NaCl$ **B** $HOCl$ **C** Cl_2O_7 **D** ClF

2 Which of the following is **not** a redox reaction?

    A $Zn(NO_3)_2(aq) + Mg(s) \rightarrow Mg(NO_3)_2(aq) + Zn(s)$
    B $U(s) + 6ClF(l) \rightarrow UF_6(l) + 3Cl_2(g)$
    C $2NO_2(g) \rightarrow N_2O_4(g)$
    D $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

3 Which of the following half-equations represents a reduction reaction?

    A $CuCl \rightarrow Cu^{2+} + Cl^- + e^-$ **C** $VO^{2+} + 2H^+ + e^- \rightarrow V^{3+} + H_2O$
    B $N_2O_4 + 2H_2O \rightarrow 2NO_3^- + 4H^+ + 2e^-$ **D** $MnO_4^{2-} \rightarrow MnO_4^- + e^-$

4 Consider the following reactions of four metals – D, Z, Q and X.

    $Q(s) + X(NO_3)_2(aq) \rightarrow Q(NO_3)_2(aq) + X(s)$ $Q(s) + Z(NO_3)_2(aq) \rightarrow Q(NO_3)_2(aq) + Z(s)$

    $Z(s) + X(NO_3)_2(aq) \rightarrow Z(NO_3)_2(aq) + X(s)$ $D(s) + Z(NO_3)_2(aq) \rightarrow D(NO_3)_2(aq) + Z(s)$

From these data it can be deduced that:

    A X is more reactive than Q   **C** Z is a stronger reducing agent than X
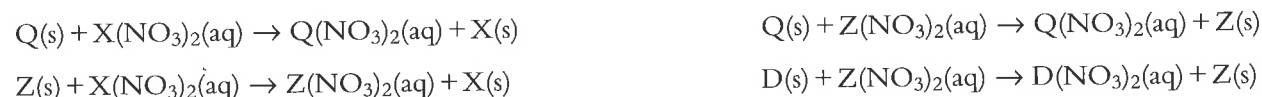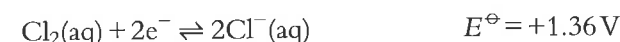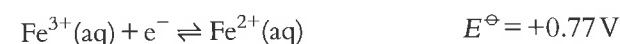   **B** Q is the most reactive metal   **D** D is a stronger reducing agent than Q

5 How many electrons are required when the following half-equation is balanced using the smallest possible integers?

    $Br_2 + H_2O \rightarrow BrO_3^- + H^+ + e^-$
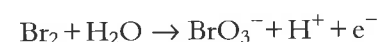
    A 2   **B** 5   **C** 10   **D** 12

HL 6 Use the following standard electrode potentials to calculate the cell potential when an $Fe^{3+}|Fe^{2+}$ half-cell is connected to a $Cl_2|Cl^-$ half-cell:

    $Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$ $E^\ominus = +0.77\,V$

    $Cl_2(aq) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E^\ominus = +1.36\,V$

    A $-0.18\,V$ **B** $+2.13\,V$ **C** $+0.59\,V$ **D** $+0.09\,V$

HL 7 Consider the following standard electrode potentials:

    $Mn^{2+} + 2e^- \rightleftharpoons Mn$ $E^\ominus = -1.18\,V$ $Pb^{2+} + 2e^- \rightleftharpoons Pb$ $E^\ominus = -0.13\,V$

    $Co^{2+} + 2e^- \rightleftharpoons Co$ $E^\ominus = -0.28\,V$ $Pd^{2+} + 2e^- \rightleftharpoons Pd$ $E^\ominus = +0.99\,V$

From these data it can be deduced that:

    A Co is a stronger reducing agent than Mn   **C** Mn is a stronger reducing agent than Pd
    B Pb^{2+} is a stronger oxidising agent than Pd^{2+} **D** Co^{2+} is a stronger reducing agent than Mn^{2+}

HL 8 Use the following standard electrode potentials to decide which reaction will be spontaneous:

    $Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$ $E^\ominus = -0.41\,V$

    $Cr^{3+} + 3e^- \rightleftharpoons Cr$ $E^\ominus = -0.74\,V$

    $Po^{2+} + 2e^- \rightleftharpoons Po$ $E^\ominus = +0.65\,V$

    $UO_2^+ + 4H^+ + e^- \rightleftharpoons U^{4+} + 2H_2O$ $E^\ominus = +0.62\,V$

    $ReO_4^- + 8H^+ + 7e^- \rightleftharpoons Re + 4H_2O$ $E^\ominus = +0.36\,V$

    A $UO_2^+ + 4H^+ + 2Po^{2+} \rightarrow U^{4+} + 2H_2O + 2Po$
    B $2Cr + 3Po^{2+} \rightarrow 2Cr^{3+} + 3Po$
    C $Re + 4H_2O + 7Cr^{3+} \rightarrow ReO_4^- + 8H^+ + 7Cr^{2+}$
    D $3U^{4+} + 6H_2O + Cr^{3+} \rightarrow Cr + 3UO_2^+ + 12H^+$
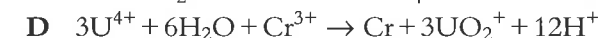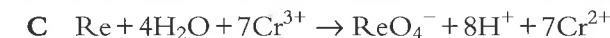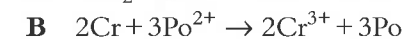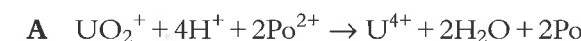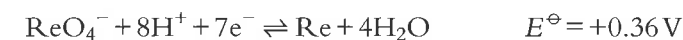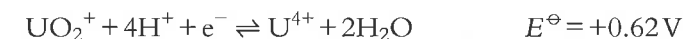
HL 9 An experiment is carried out to electroplate a key with silver. Which of the following is correct about the way the experiment is set up?

    A The cathode is made of silver and the key is the anode.
    B The electrolyte is a solution of copper sulfate.
    C The key is the cathode and the electrolyte is a silver nitrate solution.
    D The cathode is made of silver and the electrolyte is a silver nitrate solution.

HL 10 A copper sulfate solution is electrolysed for 30 minutes using platinum electrodes. 0.010 mol copper is deposited on one of the electrodes. Which of the following is correct?

    A 0.020 mol oxygen is produced at the cathode.
    B 0.010 mol oxygen is produced at the anode.
    C 0.010 mol hydrogen is produced at the cathode.
    D 0.0050 mol oxygen is produced at the anode.

11 A student carried out a redox titration to determine the amount of iron present in some iron tablets. The manufacturer claimed that each tablet contained 65 mg of iron present as iron(II) sulfate. The student crushed five tablets and heated them with sulfuric acid to dissolve the iron. The mixture was filtered and made up to a total volume of $250.0\,cm^3$ with distilled water. She then measured out $25.00\,cm^3$ of this solution, added $25.00\,cm^3$ of $1\,mol\,dm^{-3}$ sulfuric acid to acidify the solution and titrated against $5.00 \times 10^{-3}\,mol\,dm^{-3}$ KMnO4(aq) until the first permanent pink colour was seen. An average volume of $21.50\,cm^3$ of $KMnO_4(aq)$ was required for the titration.

    a Define oxidation in terms of electrons.   **[1]**

    b The *unbalanced* ionic equation for the reaction between KMnO₄ and iron(II) is:

        $MnO_4^-(aq) + H^+(aq) + Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + Fe^{3+}(aq) + H_2O(l)$
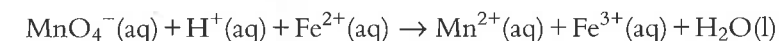
       i What is the oxidation number of Mn in MnO_4^-?   **[1]**
      ii Identify the reducing agent in this reaction.   **[1]**
     iii Balance the equation.   **[2]**

    c   **i** Calculate the number of moles of KMnO₄ that reacted.   **[1]**
      ii Calculate the number of moles of iron(II) ions that reacted with the KMnO₄   **[1]**
     iii Determine the mass of iron in an iron tablet   **[3]**
     iv Comment on the manufacturer's claim.   **[2]**

12 **a** Define a **reducing agent** in terms of electrons. [1]

    b A series of experiments was carried out in order to work out an activity series for some metals. Different metals were added to solutions of salts and the following experimental data were obtained:

	Metal	Salt solution	Observations
I	zinc	copper(II) sulfate	brown deposit formed and the blue colour of the solution fades
II	zinc	lead(II) nitrate	grey crystals formed on the piece of zinc
III	copper	lead(II) nitrate	no reaction
IV	zinc	magnesium nitrate	no reaction

      i Write an ionic equation for the reaction that occurs in experiment **I**. [2]
     ii What do the results of experiment **III** indicate about the relative reactivity of copper and lead? [1]
    iii Arrange the metals in order of reactivity, stating clearly which is the most reactive and which the least. [1]
     iv Explain which of the four metals is the strongest reducing agent. [3]
      v Write an ionic equation for the reaction between magnesium and lead nitrate. [2]

    c A voltaic cell was set up with a piece of magnesium dipping into a solution of magnesium nitrate and a piece of zinc dipping into a solution of zinc nitrate.
      i Draw a labelled diagram of the voltaic cell. Label the anode in the cell and show the direction of electron flow in the external circuit. [3]
     ii Write an ionic equation for the reaction that occurs in the zinc half-cell and classify this reaction as oxidation or reduction. [2]

13 Sodium metal can be obtained by the electrolysis of molten sodium chloride.

    a Explain why solid sodium chloride does not conduct electricity but molten sodium chloride does. [2]

    b State the name of the product at the anode in this process and write half-equations for the reactions at each electrode, stating clearly which is which. [3]

HL 14 Standard electrode potentials are measured relative to the standard hydrogen electrode.

    a Draw a labelled diagram showing the essential features of a standard hydrogen electrode. [5]

    b The diagram shows a voltaic cell:

      i Use standard electrode potentials in Table **9.7** (page **396**) to calculate the standard cell potential. [1]
     ii Write an equation, including state symbols, for the overall cell reaction. [2]
    iii Explain which electrode is the anode. [2]
     iv Show on the diagram the direction of electron flow in the external circuit. [1]
      v Explain the role of the salt bridge in this cell. [2]
     vi Calculate $\Delta G^{\ominus}$ for the cell reaction and comment on whether the reaction is spontaneous or not at 25 °C. Faraday's constant = $96\,500\,\text{C mol}^{-1}$ [3]

platinum electrode

Mn

1 mol dm⁻³ Fe²⁺
1 mol dm⁻³ Fe³⁺

1 mol dm⁻³ Mn²⁺
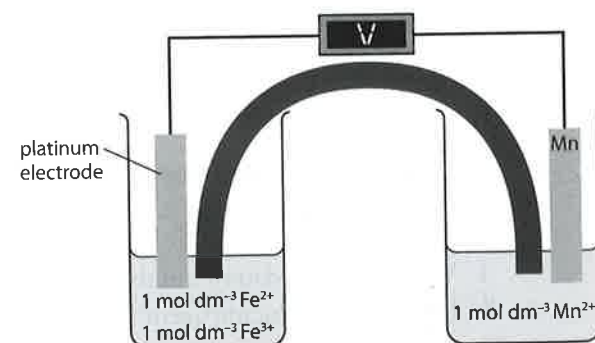
HL 15 Consider the following half-equations and standard electrode potentials:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l) \qquad E^{\ominus} = +1.51\,\text{V}$$
$$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq) \qquad E^{\ominus} = +1.36\,\text{V}$$
$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l) \qquad E^{\ominus} = +1.33\,\text{V}$$
$$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq) \qquad E^{\ominus} = +1.09\,\text{V}$$

    a Use these equations to identify, giving a reason, the strongest oxidising agent. [2]

    b A solution of acidified potassium dichromate(VI) is added to a solution containing equal concentrations of bromide ions and chloride ions. Deduce the balanced equation for the reaction that occurs. [3]

    c State and explain the sign of $\Delta G^{\ominus}$ for the following reaction:

$$2Cl^-(aq) + Br_2(l) \rightarrow Cl_2(g) + 2Br^-(aq)$$ [2]

    d Consider the unbalanced half-equation:

$$HCOOH(aq) + H^+(aq) + e^- \rightarrow HCHO(aq) + H_2O(l) \qquad E^{\ominus} = +0.06\,\text{V}$$
methanoic acid   methanal

      i State the oxidation numbers of C in HCOOH and HCHO and use these to explain whether HCOOH is oxidised or reduced. [3]
     ii Balance the half-equation. [1]
    iii Write a balanced equation for the spontaneous reaction that occurs when a solution containing MnO_4^- and H^+ is added to a solution containing methanal. [2]
     iv Explain why, when the two solutions in **iii** are mixed, a reaction may not occur. [1]

HL 16 **a** A concentrated solution of sodium chloride is electrolysed using platinum electrodes. State the products formed at the anode and the cathode and write half-equations for their formation. [4]
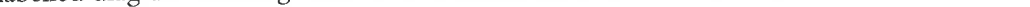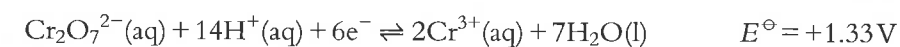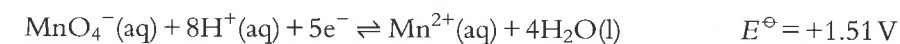
    b When a solution of copper sulfate is electrolysed using platinum electrodes, a gas is formed at one of the electrodes.
      i Identify the electrode at which the gas is formed and state an equation for its formation. [2]
     ii State two ways in which the electrolyte changes during this experiment. [2]

    c When a solution of copper sulfate is electrolysed using copper electrodes, no gas is evolved.
      i Write equations for the half-equations occurring at the anode and cathode in this cell. [2]
     ii State and explain any changes in the appearance of the electrolyte during this experiment. [2]

Summary

oxidation is gain of oxygen/loss of hydrogen
reduction is loss of oxygen/gain of hydrogen

An oxidising agent accepts electrons and thereby gets reduced.
A reducing agent donates electrons and thereby gets oxidised.

oxidation is loss of electrons
reduction is gain of electrons

When combining half-equations, make sure electrons balance.

Balancing half-equations:
1 balance all atoms except H and O
2 add H_2O to side deficient in O
3 add H^+ to side deficient in H
4 add e^- to balance charges.

Oxidation occurs at the negative electrode, the anode.
Reduction occurs at the positive electrode, the cathode.

Electrons flow through an external circuit from the more reactive metal to the less reactive metal.

salt bridge – electrical connection between two half-cells allowing ions to flow between the half-cells

voltaic cells – use redox reactions to generate electricity

cell notation:
Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)
  oxidation   reduction

HL
more negative $E^{\ominus}$ value indicates stronger reducing agent

more positive $E^{\ominus}$ value indicates stronger oxidising agent

standard electrode potential ($E^{\ominus}$) – the voltage of a half-cell connected to a standard hydrogen electrode under standard conditions

calculating cell potential: reverse sign of more negative $E^{\ominus}$ value, and add values together

positive $E^{\ominus}_{cell}$ value indicates spontaneous reaction

oxidation involves increase in oxidation number
reduction involves decrease in oxidation number

for elements always 0

in compounds usually: O=−2; H=+1

oxidation number

HL for transition metal in complex ion is worked out from charges of ligands

Transition metals and some main group elements have variable oxidation numbers.

The reactants in a redox reaction undergo a change in oxidation number.

metals:
– more reactive metal displaces less reactive one from salt solution
– more reactive metal is stronger reducing agent

activity series – metals are arranged in order of how easily they undergo oxidation

To ELECTROLYSIS on next page

The Winkler method is used for determining biochemical oxygen demand – a measure of how polluted water is.

$2H^+ + 2e^- \rightleftharpoons H_2$ $E^{\ominus} = 0.00V$

standard hydrogen electrode – H_2 bubbled past Pt electrode in $1\,mol\,dm^{-3}$ H^+ solution at 100 kPa and 298 K

Electrons flow from the half-cell with the more negative $E^{\ominus}$ value to the half-cell with the more positive one.

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

REDOX

ELECTROLYSIS – breaking down of a substance by passing electricity through it

electrical energy converted to chemical energy

Oxidation occurs at the positive electrode (anode).
Reduction occurs at the negative electrode (cathode).

reaction is non-spontaneous

Electrons flow in the external circuit, ions flow through the electrolyte.

electrolyte – solution or molten compound that will conduct electricity

In molten salts, a metal is formed at the cathode and a non-metal at the anode.

In aqueous solutions, usually a metal or hydrogen is formed at the cathode and a halogen or oxygen is formed at the anode.

HL

factors that affect which products are formed

factors that affect how much product is formed

standard electrode potentials of the species in solution

concentration of the electrolyte

material from which electrodes are made

The number of moles formed is proportional to the current and the time, and inversely proportional to the charge on the ion.

$CuSO_4$(aq) (Pt electrodes)
anode: oxygen
cathode: copper

Na_2SO_4(aq)
anode: oxygen
cathode: hydrogen

$CuSO_4$(aq) (Pt electrodes)
anode: oxygen
cathode: copper

$CuSO_4$(aq) (Cu electrodes)
anode: Cu dissolves
cathode: copper

dilute NaCl(aq)
anode: oxygen

concentrated NaCl(aq)
anode: chlorine

the same current flows through cells connected in series