CHAPTER

08 Redox reactions

Some of the most colourful and exothermic reactions are classified as redox reactions. This group of reactions includes some that are vitally important for the functioning of the human body. Redox reactions also provide the energy and produce key materials for our modern lifestyle.

In this chapter, you will learn how redox reactions can be defined in terms of electron transfer, and how this definition can be extended by using the concept of oxidation number. You will find out how to write balanced half-equations that describe the transfer of electrons, and then how to combine these half-equations to create an overall equation for the reaction. You will also become familiar with redox reactions such as metal displacement reactions.

Science understanding

- Oxidation–reduction (redox) reactions involve the transfer of one or more electrons from one species to another
- Oxidation involves the loss of electrons from a chemical species, and reduction involves the gain of electrons by a chemical species; these processes can be represented using half-equations and redox equations (acidic conditions only)
- A range of reactions involve the oxidation of one species and reduction of another species, including metal and halogen displacement reactions, combustion and corrosion
- The species being oxidised and reduced in a redox reaction can be identified using oxidation numbers

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Sample proofs

8.1 Oxidation and reduction

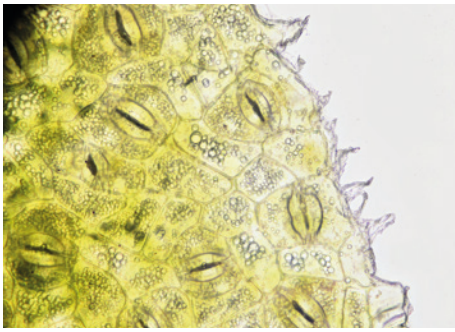

FIGURE 8.1.1 When glycerol is added to potassium permanganate, a vigorous reaction occurs in which the glycerol is oxidised by the potassium permanganate.

Everyday, you depend on a large number of chemical reactions. Many of these are redox reactions (*red*-uction; *ox*-idation). The bleaching of hair, corrosion of metals, extraction of metals from their ores, combustion of fuels, and reactions in batteries that produce electrical energy, as well as respiration and photosynthesis, are all redox reactions. The highly exothermic reaction between glycerol and potassium permanganate shown in Figure 8.1.1 is a spectacular example of a redox reaction.

In this section, you will learn how redox reactions are defined in terms of electron transfer and how to represent this transfer of electrons using half-equations.

INTRODUCING REDOX REACTIONS

Early understandings of redox reactions

When chemistry evolved from the ancient study of alchemy, many of the reactions known to early chemists involved air. French chemist Antoine Lavoisier identified the reactive component of air and named it oxygen. As a result, reactions in which oxygen was a reactant were described as oxidation reactions. In air, the combustion of an element such as carbon, sulfur or iron produces an oxide:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$$

FIGURE 8.1.2 Molten iron from a blast furnace being poured into a bucket

Because elemental iron reacts readily with oxygen, iron is generally found in nature in ores containing minerals, such as haematite (Fe_2O_3) and magnetite (Fe_3O_4). The iron metal used extensively for construction has been extracted from iron ore in a blast furnace. Pouring the molten iron from the blast furnace is shown in Figure 8.1.2.

The extraction of iron from iron ore in a blast furnace can be represented by the equation:

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)$$

In this reaction, the iron(III) oxide loses oxygen and the carbon monoxide gains oxygen. The iron(III) oxide is described as having been **reduced** and the carbon monoxide is described as having been **oxidised**.

Oxidation and reduction always occur simultaneously; hence the term 'redox reaction'.

CHEMFILE

Origins of the words 'oxidation' and 'reduction'

Scientists first used the term 'oxidation' in the late 18th century after the work of Antoine Lavoisier. Lavoisier showed that the 'burning' of metals, such as mercury, involved combining them with oxygen.

The term 'reduction' was used long before this to describe the process of extracting metals from their ores. The word 'reduction' comes from the Latin *reduco*, meaning to restore. The process of metal extraction was seen as restoring the metal from its compounds, such as iron from iron oxide or copper from copper(II) oxide. The reduction of copper(II) oxide to form copper powder occurs when copper(II) oxide is heated in the presence of hydrogen or methane gas, as shown in Figure 8.1.3. Some fine particles of copper escape with the gas, causing the green flame.

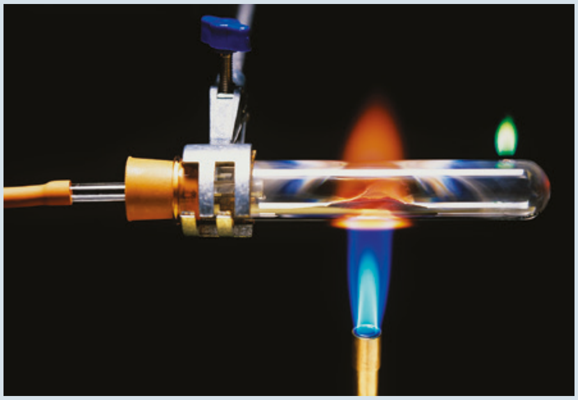

FIGURE 8.1.3 The reduction of copper(II) oxide to form copper powder occurs when copper(II) oxide is heated in the presence of hydrogen or methane gas.

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Transfer of electrons

Development of the atomic theory allowed chemists to understand oxidation and reduction reactions as electron transfer processes. The older, limited view of oxidation as the gain of oxygen was replaced by an electron transfer model that defined oxidation as the loss of electrons.

If you heat a piece of magnesium ribbon in an experiment as shown in Figure 8.1.4, it burns with a brilliant white flame. Magnesium oxide powder is formed.

FIGURE 8.1.4 Magnesium ribbon burns brightly when heated in air to form a white powder, magnesium oxide.

This reaction can be represented by the equation:

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

The reaction involves a loss and gain of electrons by the reactants, which can be represented by two **half-equations**.

Each magnesium atom loses two electrons to form a magnesium ion (Mg^{2+}). The half-equation for this part of the overall reaction is:

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

Notice that when electrons are lost, they appear as products in the half-equation.

At the same time, each oxygen atom in the oxygen molecule (O_2) gains two electrons (i.e. four electrons per oxygen molecule):

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

Notice that when electrons are gained, they appear as reactants in the half-equation. The electrons that are gained by the oxygen come from the magnesium atoms.

The burning of magnesium involves the transfer of electrons from magnesium atoms to oxygen atoms. Atoms also lose and gain electrons in many other reactions, and this transfer of electrons provides a definition of oxidation and reduction.

Redox reactions involve the transfer of electrons from one chemical species to another. Redox reactions can be considered as occurring in two halves, both happening simultaneously.

In these reactions:

- one of the reactants *loses* electrons in a process called **oxidation**
- one of the reactants *gains* electrons in a process called **reduction**.

The mnemonic OIL (Oxidation Is Loss) RIG (Reduction Is Gain) is a way to remember the difference between oxidation and reduction processes in terms of electron movement (Figure 8.1.5).

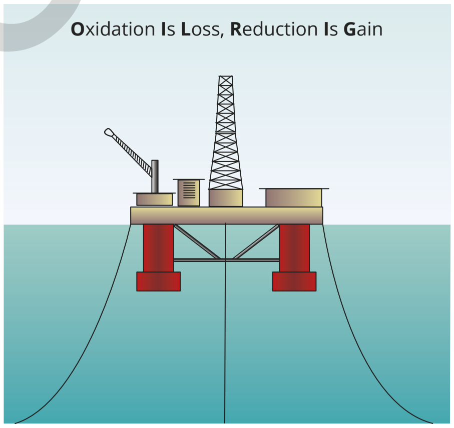

FIGURE 8.1.5 The mnemonic OIL RIG is a useful way to remember that Oxidation Is the Loss of electrons and Reduction Is the Gain of electrons.

The mnemonic OIL RIG reminds you that:

- oxidation is defined as the loss of electrons
- reduction is defined as the gain of electrons.

Other examples of redox reactions

Many redox reactions do not involve a reaction with oxygen. The reaction between potassium and chlorine shown in Figure 8.1.6 is an example:

$$2K(s) + Cl_2(g) \rightarrow 2KCl(s)$$

Oxidation half-equation: $K(s) \rightarrow K^+(s) + e^-$

Reduction half-equation: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$

Another example is the halogen displacement reaction between chlorine gas and potassium bromide solution:

$$Cl_2(g) + 2KBr(aq) \rightarrow Br_2(aq) + 2KCl(aq)$$

Oxidation half-equation: $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$

Reduction half-equation: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$

FIGURE 8.1.6 Potassium burning in chlorine gas is a spectacular example of a redox reaction.

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Worked example 8.1.1

IDENTIFYING OXIDATION AND REDUCTION

Write the oxidation and reduction half-equations for the reaction with the overall equation:

$$2NaI(aq) + Br_2(aq) \rightarrow 2NaBr(s) + I(l)$$

Thinking	**Working**
Identify the ions in the product.	NaBr is made up of Na^+ and Br^- ions.
Write the half-equation for the oxidation of the reactant that forms positive ions and balance the equation with electrons.	$Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$
Write the half-equation for the reduction of the reactant and balance the equation with electrons.	$2I^-(aq) \rightarrow I_2(aq) + 2e^-$

Note that this is an example of a halogen displacement reaction in which one halogen is oxidised (the halide ions lose electrons to produce the elemental halogen) and the other halogen is reduced to produce the halide ions. In this situation, the bromine is reduced to bromide ions.

Worked example: Try yourself 8.1.1

IDENTIFYING OXIDATION AND REDUCTION

Write the oxidation and reduction half-equations for the reaction with the overall equation:

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

Oxidising agents and reducing agents

An **oxidising agent**, or **oxidant**, enables or causes another chemical to be oxidised. Similarly, a **reducing agent**, or **reductant**, enables or causes another chemical to be reduced. Redox reactions always involve an oxidising agent and a reducing agent that react together.

In the reaction between magnesium and oxygen shown in Figure 8.1.7, magnesium is being oxidised by oxygen. So, oxygen is the oxidising agent. In turn, oxygen is gaining electrons from magnesium. It is being reduced by the magnesium, so magnesium is the reducing agent.

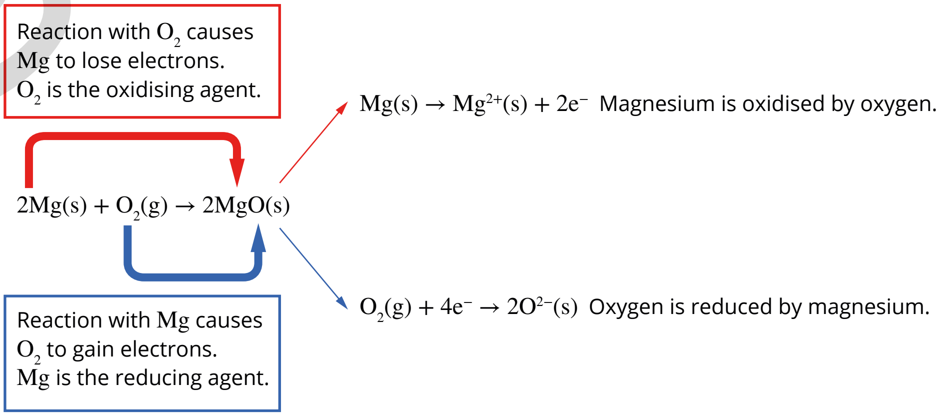
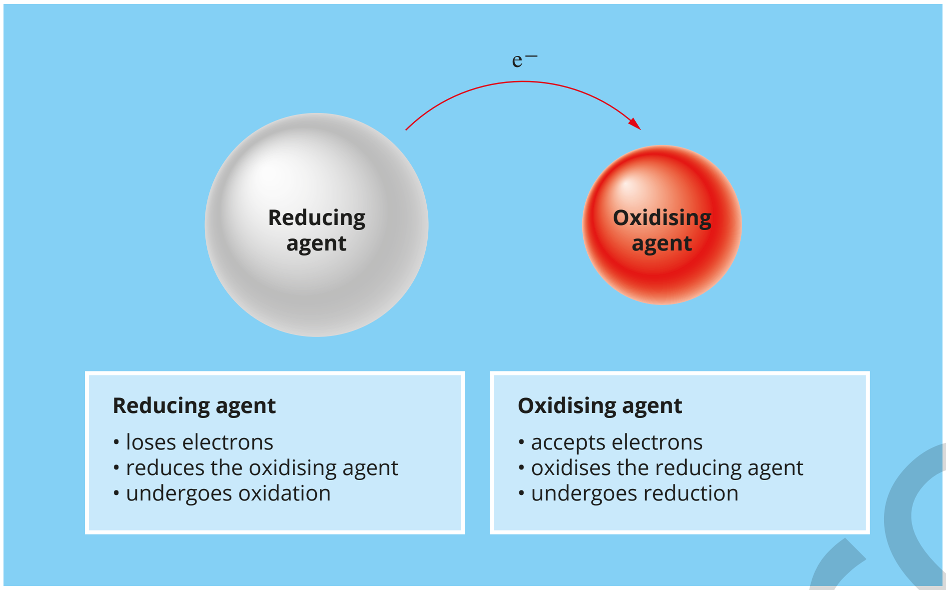


FIGURE 8.1.7 In the reaction between magnesium and oxygen, magnesium is the reducing agent and oxygen is the oxidising agent.

Since metals tend to lose electrons, they act as reducing agents, donating electrons to the substance being reduced.

Figure 8.1.8 summarises the list of redox terms introduced in this section.



Reducing agent

- loses electrons
- reduces the oxidising agent
- undergoes oxidation

Oxidising agent

- accepts electrons
- oxidises the reducing agent
- undergoes reduction

FIGURE 8.1.8 Summary of redox reaction terms

Reducing agents cause another chemical to be reduced. In the reaction, they are oxidised.

Oxidising agents cause another chemical to be oxidised. In the reaction, they are reduced.

REDOX EQUATIONS

Writing simple half-equations

Half-equations show what is happening as electrons are transferred in a redox reaction. Like other chemical equations, half-equations must be balanced so there is the same number of atoms of each element on each side of the arrow. Similarly, charge must also be balanced. Half- and overall equations should also indicate states.

In an oxidation half-equation, the electrons are 'lost' or produced so they are always written on the right-hand side of the equation.

The half-equation for the oxidation of $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$ is written as:

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

Charge is balanced by adding an electron to the right-hand side of the equation.

The half-equation for the reduction of $Cl_2(g)$ to $Cl^-(aq)$ is written as:

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

Charge is balanced by adding two electrons to the left-hand side of the equation.

For a reduction process, electrons are 'gained' by the reactant. For this to happen, the electrons must appear on the left-hand side of the equation.

Checking which side of the equation the electrons appear on allows you to determine whether a process is oxidation or reduction.

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Worked example 8.1.2

WRITING SIMPLE HALF-EQUATIONS

When sodium metal reacts with fluorine gas (F_2), solid sodium fluoride is formed.

The oxidation and reduction reactions can be represented by two half-equations. Write these half-equations and identify the substances that are oxidised and reduced.

Thinking	**Working**
Identify one reactant and the product it forms and write them on each side of an equation. Balance the equation for the element.	$F_2(g) \rightarrow 2F^-(s)$
Add electrons to balance the equation for charge.	$F_2(g) + 2e^- \rightarrow 2F^-(s)$
To decide whether the reactant is oxidised or reduced, remember that oxidation is loss of electrons and reduction is gain of electrons.	Electrons are gained, so this is reduction. The $F_2(g)$ is being reduced.
Identify the second reactant and the product it forms, and write them on each side of an equation. Balance the equation for the element.	$Na(s) \rightarrow Na^+(s)$
Add electrons to balance the equation for charge.	$Na(s) \rightarrow Na^+(s) + e^-$
To decide whether the reactant is oxidised or reduced, remember that oxidation is loss of electrons and reduction is gain of electrons.	Electrons are lost, so this is oxidation. The Na(s) is being oxidised.

Worked example: Try yourself 8.1.2

WRITING SIMPLE HALF-EQUATIONS

When a piece of copper metal is placed into a silver nitrate solution, silver metal is formed and the solution gradually turns blue, indicating the presence of copper(II) ions in solution.

The oxidation and reduction reactions can be represented by two half-equations. Write these half-equations and identify the substances that are oxidised and reduced.

Writing an overall redox equation

When writing equations for redox reactions, the two half-equations are normally written first and then added together to obtain an overall, or full, equation.

The overall equation does not show any electrons transferred; that is, no electrons appear in a properly balanced full equation. All the electrons lost in the oxidation reaction are gained in the reduction reaction. You may need to multiply one, or perhaps both, of the half-equations by a factor to ensure that the electrons balance and can be cancelled out in the overall equation.

States must be included in both redox half-equations and full equations for each species. Electrons do not have a state and should always cancel in the overall equation.

FIGURE 8.1.9 The reaction between chlorine and iron is a redox reaction. It is so exothermic that the iron burns as it reacts.

Consider the reaction of iron and chlorine shown in Figure 8.1.9. In this reaction, each Fe atom is oxidised and loses three electrons. Each Cl_2 molecule is reduced and gains two electrons:

$$Fe(s) \rightarrow Fe^{3+}(s) + 3e^-$$
$$Cl_2(g) + 2e^- \rightarrow 2Cl^-(s)$$

To write an overall equation for this reaction, the number of electrons lost during oxidation must equal the number of electrons gained during reduction. Three electrons are produced by the oxidation of an iron atom but only two electrons are required to reduce a chlorine molecule.

The lowest common multiple of 3 and 2 is 6. The half-equation involving the oxidation of Fe is multiplied by a factor of 2 to bring the total number of electrons to 6 and the half-equation involving the reduction of Cl_2 is multiplied by a factor of 3 to also bring the total number of electrons to 6:

$$2Fe(s) \rightarrow 2Fe^{3+}(s) + 6e^{-}$$

$$3Cl_2(g) + 6e^{-} \rightarrow 6Cl^{-}(s)$$

When multiplying half-equations, it is essential to multiply the coefficients of all of the species in the equation by the same factor.

The two half-equations are then added to find the overall equation:

$$2Fe(s) + 3Cl_2(g) \rightarrow 2FeCl_3(s)$$

You can see that the electrons have been cancelled from each side of the equation to give the overall equation with no electrons.

Worked example 8.1.3

WRITING OVERALL REDOX EQUATIONS FROM HALF-EQUATIONS

Sodium metal is oxidised by oxygen gas in air to form solid sodium oxide.

Write the half-equations for the reaction and hence write the balanced overall equation.

Thinking	Working
Identify one reactant and the product it forms, and write them on each side of the equation. Balance the equation for the element.	$O_2(g) \rightarrow 2O^{2-}(s)$
Add electrons to balance the equation for charge.	$O_2(g) + 4e^{-} \rightarrow 2O^{2-}(s)$
Identify the second reactant and the product it forms, and write them on each side of the equation. Balance the equation for the element.	$Na(s) \rightarrow Na^{+}(s)$
Add electrons to balance the equation for charge.	$Na(s) \rightarrow Na^{+}(s) + e^{-}$
Multiply one equation by a suitable factor to ensure that the number of electrons is balanced.	$(Na(s) \rightarrow Na^{+}(s) + e^{-}) \times 4$ $4Na(s) \rightarrow 4Na^{+}(s) + 4e^{-}$
Add the oxidation and the reduction half-equations together, cancelling out electrons so that none are in the final equation. Combine ions to create the formula of the product.	$O_2(g) + 4e^{-} \rightarrow 2O^{2-}(s)$ $4Na(s) \rightarrow 4Na^{+}(s) + 4e^{-}$ When the electrons have been cancelled, the overall equation is: $4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$

Worked example: Try yourself 8.1.3

WRITING OVERALL REDOX EQUATIONS FROM HALF-EQUATIONS

Potassium metal is oxidised by oxygen gas in air to form solid potassium oxide.

Write the half-equations for the reaction and hence write the balanced overall equation.

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CHEMISTRY IN ACTION

Photochromic sunglasses

Some people wear glasses fitted with photochromic lenses such as the glasses in Figure 8.1.10. These glasses darken in bright sunlight and become more transparent when the light intensity drops. People who wear these glasses don't need sunglasses because the photochromic lenses can reduce the amount of transmitted light by up to 80%.

Many silver compounds, including silver chloride, are sensitive to light. Tiny crystals of silver chloride are incorporated into the complex silicate-based structure of the glass used to make the photochromic lenses. On exposure to ultraviolet light, which is present in sunlight, the chloride ions are oxidised to chlorine atoms:

$$Cl^- \rightarrow Cl + e^-$$

Electrons produced from this reaction are transferred to silver ions, reducing the silver ions to metallic silver:

$$Ag^+ + e^- \rightarrow Ag$$

The silver metal formed reflects light, causing the lenses to darken, and reducing the intensity of light reaching the wearer's eyes. To prevent the silver metal and chlorine atoms immediately forming silver chloride again, tiny amounts of copper(I) chloride are also added to the glass. Copper(I) chloride reacts with the chlorine atoms, reducing the rate at which silver chloride can be re-formed:

$$Cl + Cu^+ \rightarrow Cl^- + Cu^{2+}$$

The darkening process must be reversible for the glasses to be effective. In the absence of strong sunlight, silver ions are re-formed by a redox reaction involving the silver metal and Cu^{2+} ions:

$$Cu^{2+} + Ag \rightarrow Cu^+ + Ag^+$$

As a consequence, the lenses of the glasses recover their transparency.

FIGURE 8.1.10 The lenses of these photochromic glasses darken in sunlight as a result of redox reactions involving silver chloride.

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8.1 Review

SUMMARY

- Redox (reduction–oxidation) reactions involve the transfer of electrons from one species to another.
- Oxidation and reduction always occur at the same time.
- Half-equations are used to represent oxidation and reduction.
- Oxidation is defined as the loss of electrons, e.g. $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$.
- Reduction is defined as the gain of electrons, e.g. $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$.
- The reducing agent (reductant) donates electrons to another substance, causing that substance to be reduced. The reductant is itself oxidised.
- The oxidising agent (oxidant) accepts electrons from another substance, causing that substance to be oxidised. The oxidant is itself reduced.
- Half-equations are added together to obtain the overall equation. Before adding the half-equations, it may be necessary to multiply them by a factor to balance the electrons.
- Halogen displacement reactions occur where one halogen is oxidised (the halide ions lose electrons to produce the elemental halogen) and the other halogen is reduced to produce the halide ions.

KEY QUESTIONS

1 Complete the summary about redox reactions by using the following terms: gains, loses, I_2, I^-, reduced, oxidised.
When a reducing agent, such as Fe, reacts with an oxidising agent, such as ________, an ionic compound is formed. The reducing agent __________ electrons (is ________) and at the same time the oxidising agent __________ electrons (is ________). In this case, the products are Fe^{2+} and ___________, which form FeI_2.

2 Classify each of the following half-equations as oxidation or reduction.

- **a** $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$
- **b** $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$
- **c** $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$
- **d** $Li(s) \rightarrow Li^+(aq) + e^-$
- **e** $Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$
- **f** $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$

3 Iron reacts with hydrochloric acid according to the ionic equation:
$Fe(s) + 2H^+(aq) \rightarrow Fe^{2+}(aq) + H_2(g)$

- **a** What has been oxidised in this reaction? What is the product?
- **b** Write a half-equation for the oxidation reaction.
- **c** Identify the oxidising agent.
- **d** What has been reduced in this reaction? What is the product?
- **e** Write a half-equation for the reduction reaction.
- **f** Identify the reducing agent.

4 Balance the following half-equations and then identify each as an oxidation or a reduction reaction.

- **a** $Fe(s) \rightarrow Fe^{3+}(aq)$
- **b** $K(s) \rightarrow K^+(aq)$
- **c** $F_2(g) \rightarrow F^-(aq)$
- **d** $O_2(g) \rightarrow O^{2-}(s)$

5 Name the chemicals that undergo oxidation in the following reactions.

- **a** $2Zn(s) + O_2(g) \rightarrow 2ZnO(s)$
- **b** $Ca(s) + Cl_2(g) \rightarrow CaCl_2(s)$
- **c** $Cl_2(g) + 2NaI(aq) \rightarrow I_2(aq) + 2NaCl(aq)$

6 Identify each oxidising and reducing agent in Question **5**.

7 When nickel metal reacts with copper(II) ions in an aqueous solution, nickel(II) ions are formed. Write the oxidation half-equation for the reaction.

8 The overall equation for the reaction between aluminium metal and liquid sulfur is:

$$2Al(s) + 3S(l) \rightarrow Al_2S_3(l)$$

From the overall equation, write the half-equations for the redox process and label each one as either reduction or oxidation.

9 Metal M is found to react with oxygen to form the compound M_2O_3. In a separate reaction, metal M reacted with an aqueous solution of silver nitrate ($AgNO_3$). The unbalanced and incomplete equations for the reaction between metal M and $AgNO_3$ are given below.
$Ag^+(aq) + \underline{\hspace{1.5cm}} \rightarrow Ag(s)$
$M(s) \rightarrow \underline{\hspace{1.5cm}}(aq) + \underline{\hspace{0.8cm}}e^-$
$M(s) + \underline{\hspace{1.5cm}}(aq) \rightarrow \underline{\hspace{1.5cm}}(aq) + \underline{\hspace{1cm}}Ag(s)$

- **a** Complete the half-equations and the overall equation for the reaction between metal M and silver ions, $Ag^+(aq)$.
- **b** Identify each half-equation as either reduction or oxidation.
- **c** Identify the oxidising and reducing agents for the reaction.

10 When a strip of magnesium metal is placed in a blue solution containing copper(II) ions ($Cu^{2+}(aq)$), crystals of copper appear and the solution soon becomes paler in colour.

- **a** Show that this reaction is a redox reaction by identifying the substance that is oxidised and the one that is reduced.
- **b** Write a half-equation for the oxidation reaction.
- **c** Write a half-equation for the reduction reaction.
- **d** Write an overall redox equation.
- **e** Identify the oxidising agent and the reducing agent.
- **f** Explain why the solution loses some of its blue colour as a result of the reaction.

11 Some ions, such Cu^+, can be either oxidised or reduced.

- **a** Write the formula for the product of the oxidation of Cu^+.
- **b** Write the formula for the product of the reduction of Cu^+.

12 Calcium metal that is exposed to the air forms an oxide coating.

- **a** What is the formula of calcium oxide?
- **b** What has been oxidised in this reaction?
- **c** Write a balanced half-equation for the oxidation reaction.
- **d** What has been reduced in this reaction?
- **e** Write a balanced half-equation for the reduction reaction.
- **f** Write an overall equation for this redox reaction.
- **g** Copy the following statement and fill in the blank spaces with the appropriate words.
  Calcium has been ____________ by ____________ to calcium ions. The ______________ has gained electrons from the ______________. The oxygen has been ______________ by ______________ to oxide ions. The ____________ has lost electrons to the ____________.

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8.2 Oxidation numbers

FIGURE 8.2.1 Many redox reactions involve colour changes. It is convenient to assign individual oxidation numbers to the atoms involved in redox reactions such as this.

In this section, you will learn the set of rules that chemists use to classify redox reactions. This involves assigning **oxidation numbers** to the atoms in a reaction.

You will see how oxidation numbers can be used to determine whether a reaction that does not involve the formation of ions could be classified as a redox reaction and which substances in a redox reaction have been oxidised or reduced.

You will also discover that many transition metals have multiple oxidation states and that many of these compounds can be coloured, such as in the reaction shown in Figure 8.2.1.

OXIDATION NUMBERS

In section 8.1 you looked at redox reactions that involved the production of ionic compounds from their elements. In these cases, it was relatively easy to deduce which element gained or lost electrons by considering the charge on the ions produced in the reaction. A species that was reduced gained electrons, becoming less positive, whereas the oxidised species lost electrons, becoming more positive.

For some redox reactions, it is more difficult to identify the species that are oxidised and reduced. For example, the reaction that occurs during the wet corrosion of iron metal can be represented by the half-equations:

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

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

The first half-equation shows that the iron loses electrons and is oxidised. The second half-equation represents a reduction reaction because electrons have been gained. However, it is not obvious if oxygen or hydrogen has gained these electrons.

It is possible to determine which element has been oxidised and which has been reduced in this reaction by comparing oxidation numbers before and after the reaction. Oxidation numbers can also be called oxidation states.

Oxidation numbers have no real physical meaning. However, they are a useful tool for identifying which atoms have been oxidised and which atoms have been reduced.

Oxidation number rules

Oxidation numbers are assigned to elements involved in a reaction by following a specific set of rules.

Table 8.2.1 describes the rules for determining oxidation numbers. In the examples, the oxidation number of an element is placed above its symbol. The plus or minus sign precedes the number and so distinguishes the oxidation number from the charge on an ion where the sign is generally placed after the number. For example, the oxide ion (O^{2-}) has a charge of 2– and an oxidation number of –2. While the values are the same in this instance, it is important to remember that oxidation states do not always indicate a charge on the species.

Common oxidation states of the first 36 elements in their compounds are shown in the periodic table in Figure 8.2.2. Transition metals and some non-metals can have a range of oxidation states. These are usually calculated after applying the rules for all other elements in the compound. Appendix xx includes a list of ions that you should know the names and formulas of.

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TABLE 8.2.1 Rules for determining oxidation numbers of elements in compounds

Rule	Examples
1 The oxidation number of a free (uncombined) element is zero.	$\overset{0}{Na}$, $\overset{0}{C}$, $\overset{0}{Cl_2}$, $\overset{0}{P_4}$
2 The oxidation number of a simple ion is equal to the charge on the ion.	$\overset{+1}{Na^+}$, $\overset{-1}{Cl^-}$, $\overset{+2}{Mg^{2+}}$, $\overset{-2}{O^{2-}}$, $\overset{+3}{Al^{3+}}$, $\overset{-3}{N^{3-}}$
3 In compounds, some elements have oxidation numbers that are regarded as fixed, except in a few exceptional circumstances.	
a **Main group metals** have an oxidation number equal to the charge on their ions.	Ionic compounds: $\overset{+1}{K}Cl$, $\overset{+2}{Mg}SO_4$
b Hydrogen has an oxidation number of +1 when it forms compounds with non-metals. Exception: In metal hydrides, the oxidation number of hydrogen is –1.	Compounds of H: $\overset{+1}{H_2}O$ Metal hydrides: $Na\overset{-1}{H}$, $Ca\overset{-1}{H_2}$
c Oxygen usually has an oxidation number of –2. Exceptions: In compounds with fluorine, oxygen has a positive oxidation number (because fluorine is more electronegative than oxygen—see rule 6). In peroxides, oxygen has an oxidation number of –1.	Compounds of O: $H_2\overset{-2}{O}$ Peroxides: $H_2\overset{-1}{O_2}$, $Ba\overset{-1}{O_2}$
4 The sum of the oxidation numbers in a neutral compound is zero.	$\overset{+4}{C}\overset{-2}{O_2}$
5 The sum of the oxidation numbers in a polyatomic ion is equal to the charge on the ion.	$\overset{+6}{S}\overset{-2}{O_4}{}^{2-}$, $\overset{-3}{N}\overset{+1}{H_4}{}^{+}$
6 The most electronegative element is assigned the negative oxidation number.	$\overset{+2}{O}\overset{-1}{F_2}$

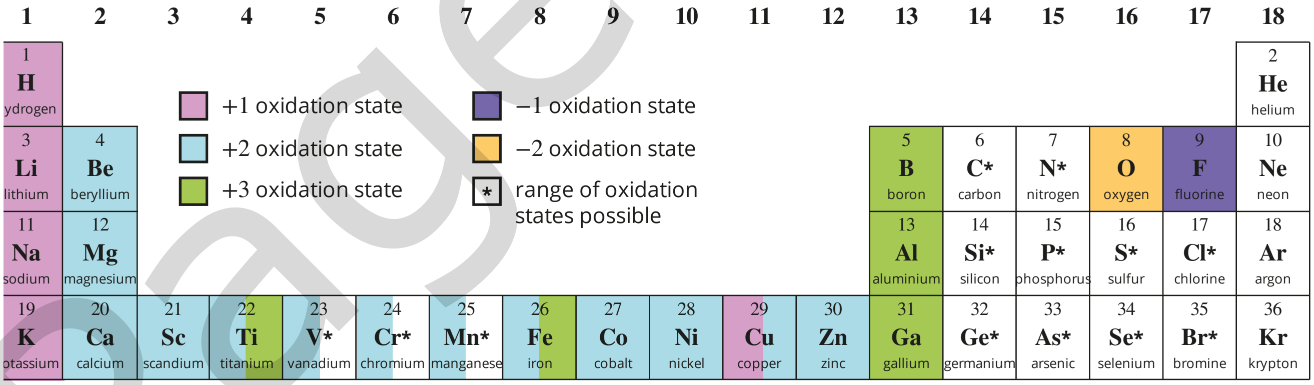

FIGURE 8.2.2 Part of the periodic table showing the most common oxidation states of some elements

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Calculating oxidation numbers

For a compound containing several elements, you can use algebra and the rules given in Table 8.2.1 to calculate the oxidation number of an element.

For example, to find the oxidation number of sulfur in H_2SO_4, there is a rule for hydrogen and for oxygen, which leaves sulfur as the only unknown. If you let the oxidation number of S equal x, the following expression can be written to solve for x:

$$\begin{aligned} (2 \times +1) + x + (4 \times -2) &= 0 \\ 2 + x - 8 &= 0 \\ x - 6 &= 0 \\ x &= +6 \end{aligned}$$

You will learn later on in this section how to use oxidation numbers to determine if a substance has been oxidised or reduced.

Worked example 8.2.1

CALCULATING OXIDATION NUMBERS

Use the rules in Table 8.2.1 to determine the oxidation number of each element in $KClO_4$.	
Thinking	**Working**
Identify an element that has a set value.	K is a main group metal in group 1. Applying rule 3a, the oxidation number of potassium is +1.
Identify any other elements that have set values.	According to rule 3c, oxygen has an oxidation number of −2 unless attached to fluorine or in a peroxide.
Use algebra to work out the oxidation number of other elements.	Let the oxidation number of chlorine in $KClO_4$ be x. Solve the sum of the oxidation numbers for x: $+1 + x + (4 \times -2) = 0$ $+1 + x - 8 = 0$ $x - 7 = 0$ $x = +7$
Write oxidation numbers above the elements in the formula.	$\overset{+1}{K}\overset{+7}{Cl}\overset{-2}{O_4}$

Worked example: Try yourself 8.2.1

CALCULATING OXIDATION NUMBERS

Use the rules in Table 8.2.1 to determine the oxidation number of each element in $NaNO_3$.

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USING OXIDATION NUMBERS

Using oxidation numbers to name chemicals

Transition elements can form ions with a number of different charges. For example, there are two compounds that can be called iron chloride: $FeCl_2$ and $FeCl_3$.

Using the rules in Table 8.2.1, you can see that the chloride ion has an oxidation number of –1. In $FeCl_2$ this means the oxidation number of iron is +2, whereas in $FeCl_3$ the oxidation number is +3.

To distinguish between the two iron chlorides, insert Roman numerals representing the appropriate oxidation number in the name.

- $FeCl_2$ is named iron(II) chloride. (Note that the old name of this substance is ferrous chloride.)
- $FeCl_3$ is named iron(III) chloride. (Note that the old name of this substance is ferric chloride.)

When naming non-metal compounds, you can also use Roman numerals to show the oxidation number of an element such as nitrogen that has several possible oxidation states. Nitrogen dioxide (NO_2) is called nitrogen(IV) oxide, while nitric oxide (NO) is called nitrogen(II) oxide. This method of naming makes it much easier to determine the formula from the name of the oxide.

For elements that can have variable oxidation states, the use of a Roman numeral in the name indicates the specific oxidation state of the element.

Using oxidation numbers to identify oxidation and reduction

You can use the concept of oxidation numbers to extend the definition of oxidation and reduction.

In this definition, a change in oxidation numbers indicates that a redox reaction has taken place. This can be used as an alternative definition of oxidation and reduction to the earlier definition involving loss and gain of electrons. It is particularly useful for non-ionic compounds when it is difficult to determine whether electrons have been transferred.

It can be stated that:

- oxidation involves an increase in oxidation number (as electrons are lost)
- reduction involves a decrease in oxidation number (as electrons are gained).

Remember that oxidation and reduction always occur together in a redox reaction.

If there is no change of oxidation number for all elements in a reaction, then the reaction is not a redox reaction.

Oxidation numbers can be used to analyse the equation of a reaction and determine whether it represents a redox process.

An increase in oxidation number indicates the element was oxidised.
A decrease in oxidation number indicates the element was reduced.

At the beginning of this chapter, you were introduced to a number of everyday redox reactions. Combustion reactions are very important redox reactions: fuel is burnt in order to produce heat while giving off CO_2 and water. The equation for the burning of carbon in excess oxygen is:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

Using oxidation numbers, you can identify both an oxidation process and a reduction process for the reaction.

$$\overset{0}{C}(s) + \overset{0}{O}_2(g) \rightarrow \overset{+4}{C}\overset{-2}{O}_2(g)$$

CHEMFILE

Colourful oxidation states

A characteristic property of the transition elements is that they form brightly coloured compounds. Different oxidation states can result in different colours for the same transition metal.

Vanadium is a very colourful transition element that has a wide variety of colours depending on its oxidation state. You can see this in Figure 8.2.3. When its oxidation state is +5, vanadium is yellow; when its oxidation state is +4, it is light blue; when its oxidation state is +3, it is green; and when its oxidation state is +2, it is magenta.

FIGURE 8.2.3 These colourful solutions have been made by adding a reducing agent (mercury–zinc amalgam) to a yellow solution containing vanadium(V) ions. The amalgam reduces the oxidation state of the vanadium by one each time it is shaken, producing, in order: blue (+4), green (+3) and magenta (+2) solutions.

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The carbon is oxidised because its oxidation number increases from 0 to +4 and the oxygen is reduced because its oxidation number decreases from 0 to −2.

The use of oxidation numbers allows you to look at a chemical reaction and determine whether it is a redox process.

Worked example 8.2.2

USING OXIDATION NUMBERS TO IDENTIFY OXIDATION AND REDUCTION IN AN EQUATION

Use oxidation numbers to determine which element has been oxidised and which has been reduced in the following equation:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

Thinking	**Working**
Determine the oxidation numbers of one of the elements on each side of the equation.	Choose C as the first element. $\overset{-4}{C}H_4(g) + 2O_2(g) \rightarrow \overset{+4}{C}O_2(g) + 2H_2O(l)$
Assess if the oxidation number has changed. If so, identify if it has increased (oxidation) or decreased (reduction).	The oxidation number of C has increased from −4 to +4, so carbon in CH_4 has been oxidised.
Determine the oxidation numbers of a second element on the left-hand and the right-hand side of the equation.	Choose oxygen as the second element. $CH_4(g) + 2\overset{0}{O}_2(g) \rightarrow C\overset{-2}{O}_2(g) + 2H_2\overset{-2}{O}(l)$
Assess if the oxidation number has changed. If so, identify if it has increased (oxidation) or decreased (reduction).	The oxidation number of O has decreased from 0 to −2, so O_2 has been reduced.
Continue this process until the oxidation numbers of all elements have been determined.	Determine the oxidation numbers of hydrogen. $C\overset{+1}{H}_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2\overset{+1}{H}_2O(l)$ The oxidation number of H has not changed (so H has not been oxidised or reduced).

Worked example: Try yourself 8.2.2

USING OXIDATION NUMBERS TO IDENTIFY OXIDATION AND REDUCTION IN AN EQUATION

Use oxidation numbers to determine which element has been oxidised and which has been reduced in the following equation:

$$CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(l)$$

Using oxidation numbers to identify conjugate redox pairs

When a half-equation is written for an oxidation reaction, the reactant, a reducing agent, loses electrons. The product is an oxidising agent. We refer to this reactant and product as a **conjugate redox pair**.

For example, in the half-equation for the oxidation of zinc:

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

zinc metal (Zn) is a reducing agent and it forms $Zn^{2+}(aq)$, an oxidising agent. Zn(s) and $Zn^{2+}(aq)$ form a conjugate redox pair $Zn(s)/Zn^{2+}(aq)$.

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When listing conjugate redox pairs, it is best to include the states of both the oxidising and reducing agent.

In the $Zn(s)/Zn^{2+}(aq)$ conjugate redox pair, the oxidation number of zinc increases from 0 to +2. The increase in the oxidation number of zinc indicates that it is an oxidation half-reaction.

For the reduction half-equation, the reactant is an oxidising agent and will gain electrons. The product formed is a reducing agent. Therefore, another conjugate redox pair is present in the redox reaction.

For example, consider the half-equation for the reduction of $Ag^+(aq)$:

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

$Ag^+(aq)$ is an oxidising agent and forms $Ag(s)$, which is a reducing agent. $Ag^+(aq)$ and $Ag(s)$ are also a conjugate redox pair. In this case, the oxidation number of silver decreases from +1 to 0, indicating that this is a reduction half-equation.

The relationship between changes in oxidation numbers and conjugate redox pairs can be seen by following the colour-coding in the equation in Figure 8.2.4. One conjugate redox pair is red and the other one is blue.

You will notice that this type of relationship is similar to the conjugate acid–base pairs that you encountered in Chapter 4. In conjugate acid–base pairs, protons are transferred. In conjugate redox pairs, electrons are transferred.

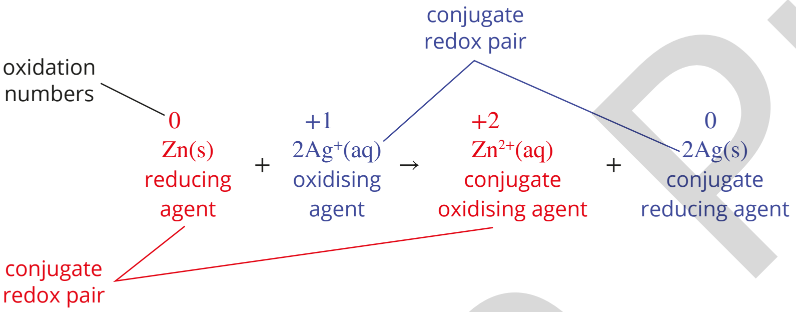

FIGURE 8.2.4 The change in oxidation numbers seen in conjugate redox pairs. For each redox reaction, there are two conjugate redox pairs.

8.2 Review

SUMMARY

- Oxidation numbers are calculated according to a set of rules.
    - Free elements have an oxidation number of 0.
    - In ionic compounds composed of simple ions, the oxidation number is equal to the charge on the ion.
    - Oxygen in a compound usually has an oxidation number of –2.
    - Hydrogen in a compound usually has an oxidation number of +1.
    - The sum of the oxidation numbers in a neutral compound is 0.
    - The sum of the oxidation numbers in a polyatomic ion is equal to the charge on the ion.
- Transition metals and some non-metals have variable oxidation numbers that can be calculated using the rules above.
- An increase in the oxidation number of an element in a reaction indicates oxidation has occurred.
- A decrease in the oxidation number of an element in a reaction indicates reduction has occurred.
- For oxidation to occur, there must be a corresponding reduction.
- If there is no change in the oxidation number of all elements in the equation for a reaction, then the reaction is not a redox reaction.

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8.2 Review *continued*

- A conjugate redox pair consists of an oxidising agent (a reactant) and the reducing agent (a product) that is formed when the oxidising agent gains electrons. In this case, the oxidation number of the oxidising agent decreases.
- The other conjugate redox pair in a redox reaction is made up of a reducing agent (a reactant) and the oxidising agent (a product) that is formed when the reducing agent loses electrons. In this case, the oxidation number of the reducing agent increases.
- Figure 8.2.5 summarises the redox terms that you need to understand from this section.

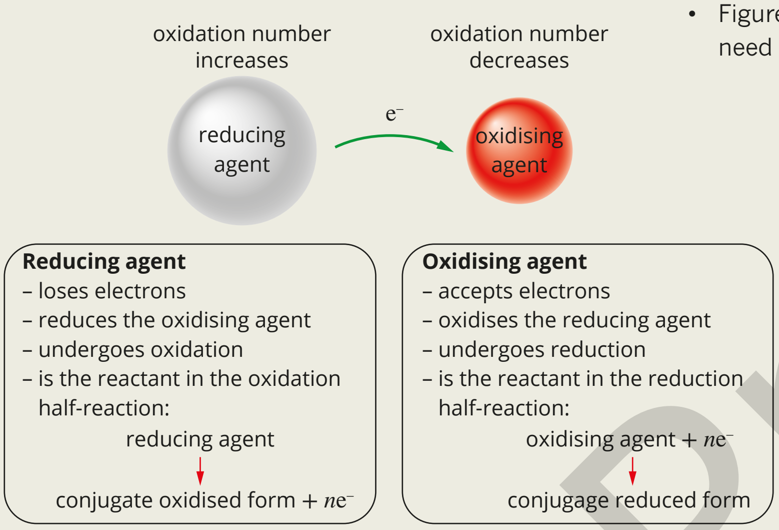

FIGURE 8.2.5 Summary of redox reaction terms

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KEY QUESTIONS

1 State the oxidation number of carbon in:
   a CO
   b CO_2
   c CH_4
   d C (graphite)
   e HCO_3^-

2 Which one or more of the following substances contain manganese in the +6 oxidation state: $MnCl_2$, $MnCl_3$, MnO_2, K_2MnO_4, $KMnO_4$?

3 Find the oxidation numbers of each element in the following compounds or ions. Hint: For ionic compounds, use the charge on each ion to help you.
   a CaO
   b $CaCl_2$
   c HSO_4^-
   d MnO_4^-
   e F_2
   f SO_3^{2-}
   g $NaNO_3$
   h $K_2Cr_2O_7$

4 Assign oxidation numbers to each element in these equations, and hence identify the oxidising agents and reducing agents.
   a $Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$
   b $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
   c $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$
   d $2Fe^{2+}(aq) + H_2O_2(aq) + 2H^+(aq) \rightarrow 2Fe^{3+}(aq) + 2H_2O(l)$

5 For each of the following redox reactions, identify the conjugate redox pairs.

Redox reaction	Conjugate redox pair (oxidation process)	Conjugate redox pair (reduction process)
$Na(s) + Ag^+(aq) \rightarrow Na^+(aq) + Ag(s)$		
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$		
$2K(s) + Cl_2(g) \rightarrow 2K^+(s) + 2Cl^-(s)$		

8.3 More complex redox equations

Not all oxidation and reduction half-equations involve simple ions and their elements. Many interesting redox reactions, such as the iodine clock reaction shown in Figure 8.3.1, involve reactants and products that have oxygen and hydrogen in their formulas. In this section, you will learn how to balance more complex half-equations in a few simple steps.

FIGURE 8.3.1 This redox reaction involving colour changes is known as the iodine clock reaction. The black compound is a starch–iodine complex.

BALANCING OXYGEN AND HYDROGEN IN HALF-EQUATIONS

Half-equations that involve atoms or simple ions can be written quite easily. For example, knowing that magnesium metal is oxidised to form Mg^{2+} ions in solution, you can readily write the half-equation as:

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

However, half-equations involving polyatomic ions are usually less obvious. For example, the anaesthetic nitrous oxide, or laughing gas (N_2O), can be prepared by the reduction of nitrate ions in an acidic solution:

$$2NO_3^-(aq) + 10H^+(aq) + 8e^- \rightarrow N_2O(g) + 5H_2O(l)$$

Such equations can be deduced from the following steps. The reduction of nitrate ions will be used to illustrate this process.

1 Balance all elements except hydrogen and oxygen in the half-equation:
$2NO_3^- \rightarrow N_2O$

2 Balance the oxygen atoms by adding water molecules to the side with fewer oxygen atoms:
$2NO_3^- \rightarrow N_2O + 5H_2O$

3 Balance the hydrogen atoms by adding H^+ ions (which are always present in acidic solution) to the side with fewer H^+ ions:
$2NO_3^- + 10H^+ \rightarrow N_2O + 5H_2O$

4 Balance the charge in the equation by adding electrons to the side that has the most positive charge:
$2NO_3^- + 10H^+ + 8e^- \rightarrow N_2O + 5H_2O$
In this case, the total charge on the left-hand side is $(2 \times -1) + (10 \times +1) = +8$. The total charge on the right-hand side is 0. Adding the 8 electrons lowers the charge of the left-hand side to match the charge on the right-hand side.

5 Add state symbols to complete the half-equation:
$2NO_3^-(aq) + 10H^+(aq) + 8e^- \rightarrow N_2O(g) + 5H_2O(l)$

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The steps outlined are for balancing redox half-equations in acidic solution only.

When writing half-equations and overall equations, it is important that they are fully balanced in terms of number of atoms and the amount of charge. Remember that the charges being equal does not mean they must be zero (Figure 8.3.2).

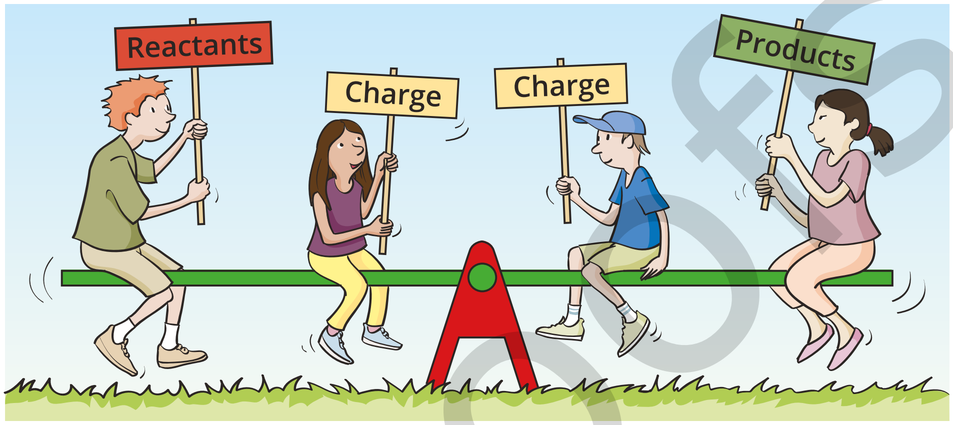

FIGURE 8.3.2 In balanced half-equations and overall equations, the number of atoms of each element is equal on both sides and the total charge on each side is equal.

The steps for balancing complex redox half-equations must be carried out in sequence for the process to work.

Worked Example 8.3.1 shows how to balance a complex redox half-equation. The final equation in this example has an overall charge of +6 for each side.

Worked example 8.3.1

BALANCING A HALF-EQUATION IN ACIDIC SOLUTION

Write the half-equation for the reduction of an acidified solution of $Cr_2O_7^{2-}$ to aqueous Cr^{3+}.

Thinking	Working
Balance all elements except hydrogen and oxygen in the half-equation.	There are 2 Cr atoms in $Cr_2O_7^{2-}$, so 2 Cr atoms are needed on the right-hand side (RHS). $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$
Balance the oxygen atoms by adding water.	There are 7 O atoms in $Cr_2O_7^{2-}$, so 7 H_2O molecules must be added to the RHS. $Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$
Balance the hydrogen atoms by adding H^+ ions. Acids provide a source of H^+ ions.	There are now 14 H atoms on the RHS and none on the left-hand side (LHS), so 14 H^+ ions must be added to the LHS. $Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$
Balance the charge in the equation by adding electrons.	The charge on the LHS is (–2) + (+14) = +12 and the charge on the RHS is 2 × +3 = +6, so 6 electrons must be added to the LHS to make the charges equal. $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
Add states to complete the half-equation.	All states are (aq) except for water, which is (l). $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

CHEMFILE

Vinegary wine or winey vinegar?

The oxidation of ethanol forms ethanoic (acetic) acid. You will learn more about this reaction in Chapter 14. Ethanoic acid is the main ingredient of vinegar and is responsible for its sourness. If a bottle of wine is left open to the atmosphere for a few days, it becomes ‘vinegary’ and undrinkable.

This reaction is put to good use when specialist vinegars such as apple cider vinegar, red wine vinegar and even beer vinegar (Figure 8.3.3) are made by deliberately oxidising the appropriate alcoholic beverage under the right conditions.

The oxidation half-equation for the production of ethanoic acid from ethanol is given by:

$$C_2H_5OH(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-$$

FIGURE 8.3.3 This selection of vinegars includes, from left to right: distilled malt vinegar, cider vinegar, white wine vinegar and malt vinegar.

Page proofs

Worked example: Try yourself 8.3.1

BALANCING A HALF-EQUATION IN ACIDIC SOLUTION

Write the half-equation for the reduction of an acidified solution of MnO_4^- to solid MnO_2.

OVERALL REDOX EQUATIONS UNDER ACIDIC CONDITIONS

To write an overall redox equation, you add the oxidation half-equation to the reduction half-equation, making sure that the number of electrons used in reduction equals the number of electrons released during oxidation. In addition, for redox reactions under acidic conditions, H^+ ions and H_2O molecules are also present as reactants and products, which need to be cancelled down.

Worked example 8.3.2

COMBINING HALF-EQUATIONS TO WRITE OVERALL REDOX EQUATIONS UNDER ACIDIC CONDITIONS

Write balanced oxidation and reduction half-equations for the reaction in which $C_2H_5OH(aq)$ and $Cr_2O_7^{2-}(aq)$ react to form $CH_3COOH(aq)$ and $Cr^{3+}(aq)$. Then write the overall redox equation for the reaction.

Thinking	**Working**
Identify one reactant and the product it forms, and write the balanced half-equation.	$C_2H_5OH(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-$
Identify the second reactant and the product it forms, and write the balanced half-equation.	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
Multiply one or both equation(s) by a suitable factor to ensure that the number of electrons on both sides of the arrow is equal.	Lowest common multiple = 12 $3 \times [C_2H_5OH(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-]$ $2 \times [Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)]$ $3C_2H_5OH(aq) + 3H_2O(l) \rightarrow 3CH_3COOH(aq) + 12H^+(aq) + 12e^-$ $2Cr_2O_7^{2-}(aq) + 28H^+(aq) + 12e^- \rightarrow 4Cr^{3+}(aq) + 14H_2O(l)$
Add the oxidation and the reduction half-equations together, cancelling electrons so that none appear in the final equation. Also cancel H_2O and H^+ if these occur on both sides of the arrow.	$3C_2H_5OH(aq) + \cancel{3H_2O(l)} \rightarrow 3CH_3COOH(aq) + \cancel{12H^+(aq)} + \cancel{12}e^-$ $2Cr_2O_7^{2-}(aq) + \overset{16H^+}{\cancel{28H^+}}(aq) + \cancel{12}e^- \rightarrow 4Cr^{3+}(aq) + \overset{11H_2O}{\cancel{14H_2O}}(l)$ $3C_2H_5OH(aq) + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \rightarrow 3CH_3COOH(aq) + 4Cr^{3+}(aq) + 11H_2O(l)$

Worked example: Try yourself 8.3.2

COMBINING HALF-EQUATIONS TO WRITE OVERALL REDOX EQUATIONS UNDER ACIDIC CONDITIONS

Write balanced oxidation and reduction half-equations for the reaction in which $SO_3^{2-}(aq)$ and $ClO^-(aq)$ react to form $H_2S(g)$ and $ClO_3^-(aq)$. Then write the overall equation for the reaction.

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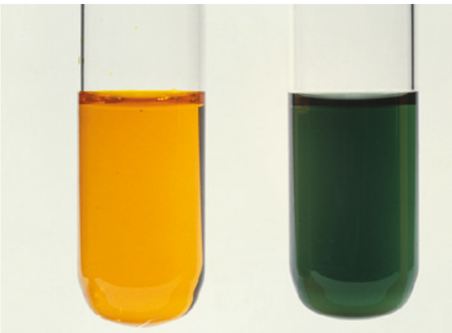

FIGURE 8.3.4 The oxidation of ethanol, described in Worked Example 8.3.2, was the basis of an older form of the breathalyser. The presence of alcohol in a motorist's breath was identified by a colour change in the oxidising agent, potassium dichromate. During the reaction, the yellow-orange colour of dichromate ions changed to the green colour of chromium(III) ions as the alcohol was oxidised.

Some strong oxidising agents such as potassium dichromate are highly coloured. The change in colour that occurs as the redox process proceeds can be used for a number of chemical analyses.

The reaction of an alcohol with acidified dichromate as seen in Worked Example 8.3.2 can be followed by the colour change of the solution from orange to green (Figure 8.3.4). This colour change was the basis for older forms of handheld breathalysers used for testing the blood alcohol level of drivers.

Page Proofs

CHEMISTRY IN ACTION

Alcohol and the road toll

Drinks such as wine, beer, vodka and bourbon contain ethanol (CH_3CH_2OH). Ethanol acts as a depressant, slowing the functioning of the brain. When alcoholic drinks are consumed in excess, their intoxicating qualities can lead to antisocial behaviour and can damage a person's health.

Because ethanol slows reaction time, it seriously affects a person's driving skills. It is estimated that nationally, alcohol has contributed to nearly 40% of all road accidents. Governments have responded by introducing penalties, such as fines and licence disqualification, for drivers whose blood alcohol concentration exceeds a certain level—typically 0.05%(m/v) (mass in grams dissolved in 100 mL of solution, or 0.05 g of alcohol in 100 mL of blood). Probationary or P-plate drivers are required to have a zero blood alcohol level.

It is difficult to determine your blood alcohol concentration because it is affected by how much alcohol you drink, how quickly or slowly you have consumed alcohol, how much you have eaten, your body mass and level of fitness and even how healthy your liver is. As a guide, to keep within a safe limit, men should not drink more than two standard drinks in the first hour and one standard drink every following hour, while women should not drink more than one standard drink every hour.

The ethanol content of alcoholic drinks varies, so it can be difficult to determine what a standard drink is. Regulations require that the ethanol content of alcoholic drinks be specified on their labels, because ethanol content determines how much drink can be consumed without adverse effects. The relationships between the type of alcoholic beverage, its ethanol content and the number of standard drinks are shown in Table 8.3.1.

TABLE 8.3.1 Typical ethanol contents of some alcoholic beverages, and a standard drink

Drink	Volume (mL)	Ethanol content (%v/v)	Number of standard drinks
Mid-strength beer, glass	285	3–4	0.8
Mid-strength beer, can	375	3–4	1
Full-strength beer, glass	285	4–6	1
Full-strength beer, can	375	4–6	1.5
Pre-mixed drink	375	5	1.5
Wine	100	10–14	1
Spirits (brandy, whisky, gin, vodka etc.)	30	37–43	1

WA Road Safety Commission

The introduction of penalties, a policy of randomly testing motorists for blood alcohol level, and various advertising campaigns have all helped to increase public awareness of the link between alcohol consumption and road accidents. However, despite 20 years of anti-drink driving messaging, alcohol still remains a factor in a quarter of fatal crashes in Western Australia.

FIGURE 8.3.5 Breathalysers are used to analyse the blood alcohol content of motorists. The sensor detects the change in colour as the ethanol is oxidised to ethanoic acid in the presence of acidified potassium dichromate.

Chemists were involved in the invention of the breathalyser, an instrument designed for police to use to estimate blood alcohol content (Figure 8.3.5). Rather than analysing samples of blood, this instrument measures the concentration of alcohol in a person's breath, which is closely related to the concentration of alcohol in their blood.

If this screening test indicates that a driver's blood is over 0.05%(m/v), more accurate measurements are taken either in a 'booze bus' or at a police station. The blood alcohol content may then be confirmed by instrumental techniques such as infrared spectroscopy or gas–liquid chromatography. Some police departments also use alcohol fuel cell sensors.

The first breathalysers operated by detecting the colour change that occurs when ethanol reacts with an acidified solution of potassium dichromate ($K_2Cr_2O_7$), forming Cr^{3+} ions and ethanoic acid. The redox reaction can be represented by the equation:

$$\underset{\text{orange}}{2Cr_2O_7^{2-}(aq)} + 3CH_3CH_2OH(g) + 16H^+(aq) \rightarrow \underset{\text{green}}{4Cr^{3+}(aq)} + 3CH_3COOH(aq) + 11H_2O(l)$$

CHEMFILE

Elephant's toothpaste

Hydrogen peroxide is such a strong oxidising agent that it can even oxidise itself, decomposing to form water and oxygen gas:

$$H_2O_2(aq) + H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

In this reaction the two half-equations are:

$$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$$

$$H_2O_2(aq) \rightarrow O_2(g) + 2H^+(aq) + 2e^-$$

The decomposition reaction of hydrogen peroxide is the basis for the impressive 'foam column' or 'elephant's toothpaste' demonstration.

When detergent and a catalyst are added to concentrated hydrogen peroxide solution, a column of foam is formed (Figure 8.3.6).

FIGURE 8.3.6 The 'elephant's toothpaste' demonstration involves a redox reaction in which hydrogen peroxide reacts with itself to form water and oxygen gas. In this reaction, the hydrogen peroxide is both the reducing agent and the oxidising agent. In this image, solid potassium iodide catalyst is added to hydrogen peroxide solution. Red colouring has also been added for effect.

Page Proofs

8.3 Review

SUMMARY

- Half-equations are used to represent oxidation and reduction.
- Half-equations are added together to obtain the overall equation. Before adding the half-equations, you may need to multiply them by a factor to balance the electrons.
- State symbols should always be included in half-equations and balanced equations for overall redox reactions.
- To balance redox half-equations under acidic conditions:
  1 Balance all atoms except hydrogen and oxygen.
  2 Balance the oxygen atoms by adding water molecules.
  3 Balance the hydrogen atoms by adding H^+ ions.
  4 Balance the charge by adding electrons.
  5 Add states.
- To write an overall equation, add the oxidation half-equation and the reduction half-equation, making sure that the number of electrons used in reduction equals the number of electrons released during oxidation.
- When combining oxidation and reduction half-equations under acidic conditions, any $H^+(aq)$ and $H_2O(l)$ that appear on both sides of the arrow should be cancelled down.

KEY QUESTIONS

1 Write half-equations for the:
  a reduction of MnO_2 to Mn^{2+}
  b reduction of MnO_4^- to MnO_2
  c reduction of SO_4^{2-} to H_2S
  d oxidation of SO_2 to SO_4^{2-}
  e oxidation of H_2S to S
  f oxidation of SO_3^{2-} to SO_4^{2-}.

2 When zinc powder is sprinkled into an acidified solution of potassium dichromate, a reaction occurs that produces zinc ions and chromium(III) ions in solution.
  a Write the oxidation half-equation for the reaction.
  b Write the reduction half-equation for the reaction.
  c Use your answers to parts **a** and **b** to write a balanced equation for the overall reaction.

3 Write the half-equations and the balanced overall equation for the reaction in which a solution containing:
  a iron(II) ions is oxidised by an acidified solution containing dichromate ions ($Cr_2O_7^{2-}$). The products include iron(III) and chromium(III) ions
  b sulfite ions (SO_3^{2-}) reacts with an acidified solution of permanganate ions (MnO_4^-) to produce a colourless solution containing sulfate ions and manganese(II) ions
  c manganese dioxide (MnO_2) reacts with concentrated hydrochloric acid to form chlorine gas and a solution containing manganese(II) ions.

4 The following equations are not balanced. For each equation:
  i identify the species that has been reduced and the species that has been oxidised
  ii write balanced half-equations for the oxidation and reduction reactions
  iii combine the half-equations to write a balanced overall equation.
    a $Ce^{4+}(aq) + H_2S(g) \rightarrow Ce^{3+}(aq) + S(s) + H^+(aq)$
    b $NO_3^-(aq) + H^+(aq) + Cu(s) \rightarrow NO(g) + H_2O(l) + Cu^{2+}(aq)$
    c $H_2O_2(aq) + Br^-(aq) + H^+(aq) \rightarrow Br_2(l) + H_2O(l)$
    d $MnO_2(s) + H^+(aq) + S(s) \rightarrow Mn^{2+}(aq) + H_2O(l) + SO_2(g)$

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8.4 The reactivity series of metals

When metals undergo corrosion, some react quickly with oxygen and water, and even more vigorously with acids. For example, magnesium ribbon reacts vigorously in acid. Other metals react quite slowly with oxygen. For example, copper pipes oxidise slowly in air, producing a brown-black copper(II) oxide coating. These are both redox reactions.

In this section, you will examine the reactivity of different metals and learn how to write equations for the displacement reactions between metals and solutions of metal ions.

REACTIVITY OF METALS

Sodium, magnesium and iron are metals that are relatively easily oxidised. Sodium is oxidised so readily that it has to be stored under paraffin oil to prevent it from reacting with oxygen in the atmosphere. The oxidation of iron, which can eventually result in the formation of rust, can be an expensive problem. For example, in 2008, corroded pipelines caused an explosion at a gas processing plant on Varanus Island. This crisis resulted in 35% of Western Australia's gas supply being lost for 2 months.

Other metals do not corrode as readily. For example, platinum and gold are sufficiently inert to exist as pure elements in nature.

Figure 8.4.1 shows a comparison of four different metals reacting with dilute acid. By observing how readily metals react with oxygen, water, dilute acids and other metal salts, it is possible to determine an order of reactivity of metals.

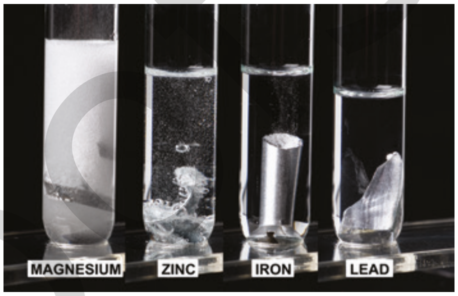
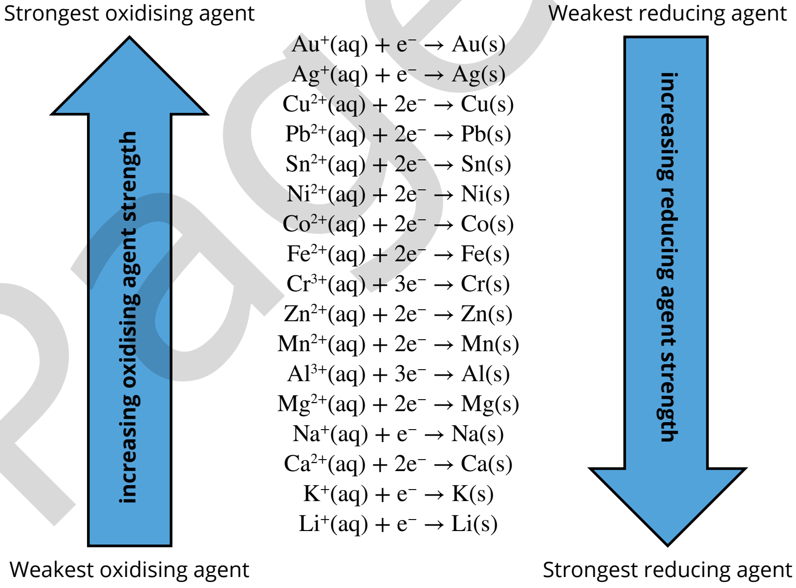


FIGURE 8.4.1 Some metals react with dilute acid to form a salt and hydrogen gas. The reaction between magnesium and dilute acid is extremely vigorous. The reaction between zinc and dilute acid is less vigorous. The reaction between iron and dilute acid is very slow. There is no reaction between lead and dilute acid. This information can be used to determine that the order of metal reactivity from most reactive to least reactive is magnesium, zinc, iron and lead.

The metals can be ranked in a list according to their reactivity, or ability to act as reducing agents. Figure 8.4.2 shows such a ranking, which is also known as a **reactivity series**. The series shows the reduction half-equations for the metal cations as each cation gains electrons to form the corresponding metal.

The metals are listed on the right-hand side of the series, from the least reactive (Au) at the top to the most reactive (K and Li) at the bottom. The lower down the table a metal is placed, the more reactive it is.

Metals, with their small number of valence electrons, act as reducing agents. A relatively small amount of energy is required to remove these valence electrons. In general, the lower the amount of energy required to remove the valence electrons, the more readily a metal will act as a reducing agent.



$Au^{+}(aq) + e^{-} \rightarrow Au(s)$
$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$
$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$
$Pb^{2+}(aq) + 2e^{-} \rightarrow Pb(s)$
$Sn^{2+}(aq) + 2e^{-} \rightarrow Sn(s)$
$Ni^{2+}(aq) + 2e^{-} \rightarrow Ni(s)$
$Co^{2+}(aq) + 2e^{-} \rightarrow Co(s)$
$Fe^{2+}(aq) + 2e^{-} \rightarrow Fe(s)$
$Cr^{3+}(aq) + 3e^{-} \rightarrow Cr(s)$
$Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$
$Mn^{2+}(aq) + 2e^{-} \rightarrow Mn(s)$
$Al^{3+}(aq) + 3e^{-} \rightarrow Al(s)$
$Mg^{2+}(aq) + 2e^{-} \rightarrow Mg(s)$
$Na^{+}(aq) + e^{-} \rightarrow Na(s)$
$Ca^{2+}(aq) + 2e^{-} \rightarrow Ca(s)$
$K^{+}(aq) + e^{-} \rightarrow K(s)$
$Li^{+}(aq) + e^{-} \rightarrow Li(s)$

FIGURE 8.4.2 The reactivity series of metals

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As you go down the reactivity series of metals in Figure 8.4.2, the:

- metals, which are on the right-hand side, become more reactive. This means the metals lower in the series are easier to oxidise and are therefore stronger reducing agents
- metal cations, which are on the left-hand side, become increasingly harder to reduce and are therefore less reactive. Cations higher in the series have a greater attraction for electrons so they are easier to reduce and are therefore relatively strong oxidising agents.

CHEMISTRY IN ACTION

The ages of discovery

Since the beginning of civilisation, human progress has depended on the discovery and development of materials. The epochs of civilisation are commonly described as:

- Stone Age
- Bronze Age
- Iron Age
- Modern Age.

As the electrochemical reactivity series shows, the first metals discovered are low in reactivity and are found as pure elements. With the discovery of fire, small samples of metals such as copper and tin, which were reduced from their ores, were found in the ashes of campfires. The mixture of copper and tin that produced the hard alloy bronze initiated the Bronze Age. Copper could be beaten into shapes for tools and weapons that held a sharper edge, and was easily resharpened once blunt. The Trojan War was conducted by bronze-shielded warriors throwing bronze-tipped spears.

Lead and iron, which are more reactive metals, require higher temperatures to extract them from their ores and efficient production methods were invented much later. Wood fires could not reach high enough temperatures. Only when charcoal was used was the manufacture of iron possible and iron weapons could be produced at a fraction of the cost of those made from bronze.

Highly reactive metals, such as aluminium and sodium, are so easily oxidised and have such stable cations that it was not until electricity was invented in the late 1800s that they could be extracted from their mineral ores.

It was so difficult to extract aluminium metal that Napoleon III proudly displayed a small bar of the metal with his crown jewels in 1855. Modern electrolytic production methods use direct current electricity to produce the metals from molten minerals. (You will encounter some of these processes in Chapter 10.) Consequently, these metals tend to be expensive to produce. Aluminium is produced using the electrolytic cells shown in Figure 8.4.3.

Historians may one day label our Modern Age as the Silicon, Aluminium, Plastics, Ceramics or Nanoparticle Age in recognition of the influence that these technologically advanced materials have had on our modern life. Further developments in materials technology will no doubt see the production of new materials to meet the demands of our modern culture.

FIGURE 8.4.3 A row of electrolytic cells used for the modern production of aluminium

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Metal displacement reactions

The order in which metals and their metal ions appear in the reactivity series enables you to predict which metals will **displace** other metals from solutions of their ions. Such reactions are known as **metal displacement reactions**.

A more reactive metal will be oxidised by, and donate its electrons to, the cation of a less reactive metal. The cation receives the electrons and is reduced. In other words, for a naturally occurring **spontaneous redox reaction** to occur, the metal ions of one metal must be above the other metal in the reactivity series as shown in Figure 8.4.4. The more reactive metal acts as the reducing agent, and the metal ions of the other metal act as the oxidising agent.

In Chapter 9 you will see how this idea of predicting whether reactions will occur can be extended to other oxidising and reducing agents by using a more wide-ranging electrochemical series.

A metal ion higher in the reactivity series (an oxidising agent) will react with a metal lower in the reactivity series (a reducing agent).

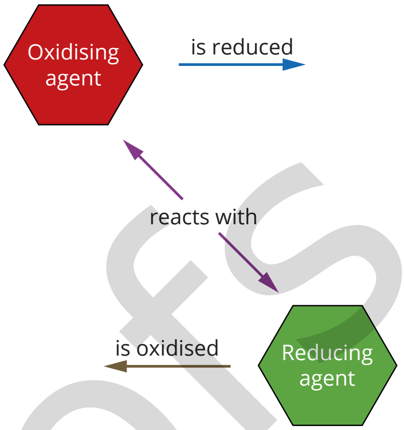

FIGURE 8.4.4 Predicting the reaction between an oxidising agent and a reducing agent

When copper wire is placed in a solution of silver nitrate as shown in Figure 8.4.5, silver ions are reduced to silver atoms by copper atoms. The silver atoms are deposited as silver crystals. The copper atoms are oxidised to form a blue solution containing copper(II) ions. As a result of the reaction, copper(II) ions have displaced silver ions from the solution.

Silver ions have oxidised copper atoms, consistent with their order in the reactivity series, as shown in Figure 8.4.6. The overall redox reaction can be represented by the equation:

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

FIGURE 8.4.5 In the flask on the left, copper wire is suspended in a solution of silver nitrate. Long crystals of silver metal are forming. In the flask on the right, the copper has displaced the silver from the solution.

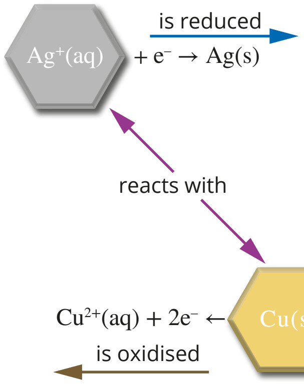

FIGURE 8.4.6 A spontaneous redox reaction occurs when copper is added to a solution of silver nitrate. Silver ions oxidise copper atoms.

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Worked example 8.4.1

PREDICTING METAL DISPLACEMENT REACTIONS

Predict whether zinc will displace copper from a solution containing copper(II) ions. If appropriate, write the overall redox equation for the reaction.

Thinking	Working
Locate the metal and the metal ions in the reactivity series.	Metals (reducing agents) are found on the right-hand side of the reactivity series and metal ions (oxidising agents) are on the left-hand side of the reactivity series. $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $Sn^{4+}(aq) + 2e^- \rightarrow Sn(aq)$ $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$ $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ $Co^{2+}(aq) + 2e^- \rightarrow Co(s)$ $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ $Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$ $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$
Determine whether the metal element is below the metal ion in the table. If this is the case, there will be a reaction.	You can see from the reactivity series that Zn is below Cu^{2+}, so there will be a reaction as shown in Figure 8.4.7.
Write the reduction half-equation for the metal ion directly as it is written in the reactivity series. Include state symbols.	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
Write the oxidation half-equation for the metal with the metal on the left-hand side of the arrow (as a reactant). Include state symbols.	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
Combine the two half-equations, balancing electrons, to give the overall equation for the reaction.	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Worked example: Try yourself 8.4.1

PREDICTING METAL DISPLACEMENT REACTIONS

Predict whether copper will displace gold from a solution containing gold ions. If appropriate, write the overall redox equation for the reaction.

According to the reactivity series, a metal displacement reaction is predicted to occur when zinc is added to copper(II) sulfate solution, as shown in Figure 8.4.7.

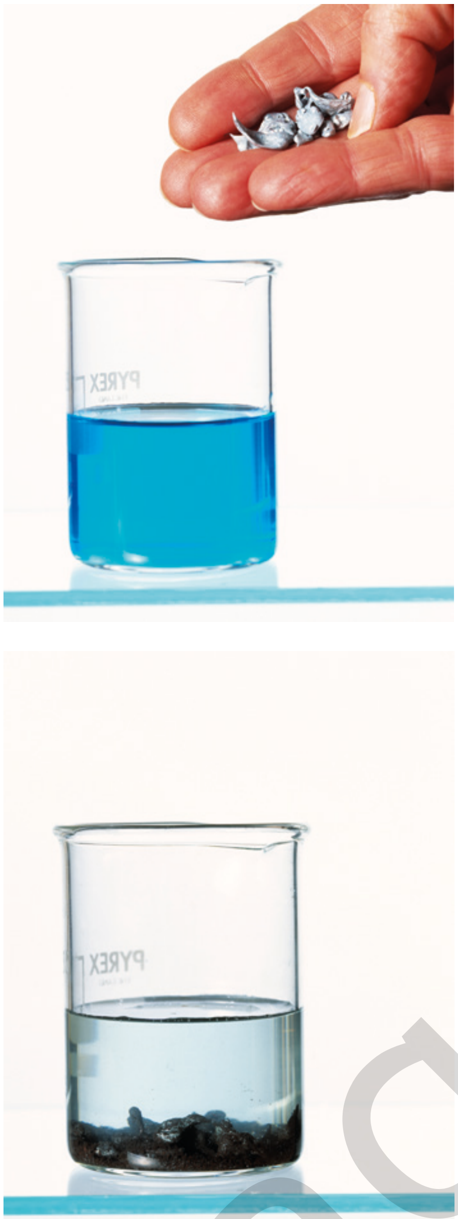

FIGURE 8.4.7 A brown deposit of copper metal is observed forming on the zinc and the blue copper(II) sulfate solution gradually becomes colourless as the concentration of Cu^{2+} ions decreases.

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8.4 Review

SUMMARY

- The reactivity series lists half-equations involving metals and their corresponding cations.
- The half-equations involving stronger oxidising agents (the ones more easily reduced) appear higher in the reactivity series than those involving weaker oxidising agents.
- The half-equations involving stronger reducing agents (the ones more easily oxidised) appear lower in the reactivity series.
- The reactivity series can be used to predict whether a redox reaction is likely to occur.
- Metal displacement reactions involve the transfer of electrons from a more reactive metal to the positive ions of a less reactive metal in solution.

KEY QUESTIONS

1 Refer to the reactivity series and predict whether each of the following reactions will spontaneously occur.

- **a** Silver metal is placed in a copper(II) nitrate solution.
- **b** A strip of aluminium is placed in a sodium chloride solution.
- **c** Magnesium is added to a solution of iron(II) sulfate.
- **d** The element zinc is placed in a tin(II) sulfate solution.
- **e** A piece of tin is placed in a silver nitrate solution.
- **f** Lead(II) nitrate solution is poured into a beaker containing zinc granules.
- **g** Gold foil is added to a lead(II) nitrate solution.

2 Use the reactivity series to predict whether a reaction will occur in each of the following situations. Write an overall redox equation for each reaction that you predict will occur.

- **a** Copper(II) sulfate solution is stored in an aluminium container.
- **b** Sodium chloride solution is stored in a copper container.
- **c** Silver nitrate solution is stored in a zinc container.

3 Solutions of zinc nitrate, tin(II) nitrate and copper(II) nitrate have been prepared in a laboratory, but are unlabelled. Name two metals that could be used to identify each solution.

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Chapter review

KEY TERMS

conjugate redox pair
displace
half-equation
main group metal
metal displacement reaction
oxidant
oxidation
oxidation number
oxidised
oxidising agent
reactivity series
redox reaction
reduced
reducing agent
reductant
reduction
spontaneous redox reaction
transition element

Oxidation and reduction

1 Define oxidation and reduction in terms of the transfer of:
   - **a** oxygen
   - **b** electrons.

2 State whether each of the statements is true or false.
   - **a** Groups 1 and 2 metal ions, such as Na^+, are reducing agents because they tend to lose electrons.
   - **b** Group 17 molecules, such as I_2, can be oxidising agents or reducing agents.
   - **c** Non-metal ions, such as Cl^-, can be reducing agents because they can lose electrons.
   - **d** Metals, such as Cu, can be oxidising agents because they can gain electrons.

3 Complete the following sentences, which describe oxidation and reduction.

Oxidation and reduction occur together. Oxidation occurs when an atom ____________ electrons to form a ___________ ion, such as happens when a calcium atom, with an electronic configuration of 2,8,8,2 ______________ electrons to form a Ca^{2+} ion. Reduction occurs when an atom _____________ electrons to form a _____________ ion or a cation __________ electrons to become a neutral atom. An example is when a bromine atom, with ___________ electrons in its valence shell, __________ an electron to form a ___________ ion.

4 Lead metal is oxidised to form Pb^{2+} ions by reaction with silver ions in solution. Write half-equations for the reaction and then write the balanced overall equation.

5 Classify each of the following half-equations as either oxidation or reduction half-equations.
   - **a** $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$
   - **b** $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$
   - **c** $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
   - **d** $K(s) \rightarrow K^+(aq) + e^-$
   - **e** $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$
   - **f** $I_2(aq) + 2e^- \rightarrow 2I^-(aq)$

6 Each of the following half-equations have a mistake in them. For each half-equation, state what the error is and then write the correct half-equation.
   - **a** $Ag(s) + e^- \rightarrow Ag^+(aq)$
   - **b** $Cu(s) + e^- \rightarrow Cu^{2+}(aq) + 3e^-$
   - **c** $Zn(aq) \rightarrow Zn^{2+}(s) + 2e^-$
   - **d** $I_2(aq) + e^- \rightarrow I^- (aq)$
   - **e** $Na^+(aq) - e^- \rightarrow Na(s)$

7 Identify the reducing agent in each of these redox reactions.
   - **a** $2Cu(s) + O_2(g) \rightarrow 2CuO(s)$
   - **b** $F_2(g) + 2LiBr(aq) \rightarrow Br_2(aq) + 2LiF(aq)$
   - **c** $2Fe^{3+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + 2Fe^{2+}(aq)$
   - **d** $2Ag^+(aq) + Ni(s) \rightarrow Ni^{2+}(aq) + 2Ag(s)$

8 Balance these half-equations.
   - **a** $Ag^+(aq) \rightarrow Ag(s)$
   - **b** $Cu(s) \rightarrow Cu^{2+}(aq)$
   - **c** $Zn(s) \rightarrow Zn^{2+}(aq)$

9 Which one of the following redox equations has not been balanced correctly?
   - **A** $Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$
   - **B** $Fe^{2+}(aq) + Zn(s) \rightarrow Fe(s) + Zn^{2+}(aq)$
   - **C** $Ag^+(aq) + Cu(s) \rightarrow Ag(s) + Cu^{2+}(aq)$
   - **D** $Zn^{2+}(aq) + Mg(s) \rightarrow Zn(s) + Mg^{2+}(aq)$

Oxidation numbers

10 What is the oxidation number of sulfur in each of the following compounds?
   - **a** SO_2
   - **b** H_2S
   - **c** H_2SO_4
   - **d** SO_3
   - **e** Na_2SO_3
   - **f** $Na_2S_2O_3$

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11 Complete the following table.

Compound	Element	Oxidation number
$CaCO_3$	Ca	
HNO_3	O	
H_2O_2		–1
HCO_3^-		+4
HNO_3	N	
$KMnO_4^-$	Mn	
H_2S	S	
Cr_2O_3	Cr	
N_2O_4	N	

12 Place the following substances in order of increasing oxidation states of nitrogen.

NO, K_3N, N_2O_4, N_2O, $Ca(NO_3)_2$, N_2O_3, N_2

13 Which of the following reactions are redox reactions? Give reasons for each of your answers.

- **a** $BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$
- **b** $2Ag + Cl_2 \rightarrow 2AgCl$
- **c** $2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$
- **d** $ZnCO_3 \rightarrow ZnO + CO_2$
- **e** $HPO_3^{2-} + I_2 + OH^- \rightarrow H_2PO_4^- + 2I^-$
- **f** $2Cu^+ \rightarrow Cu^{2+} + Cu$
- **g** $CaF_2 \rightarrow Ca^{2+} + 2F^-$
- **h** $P_4 + 6H_2 \rightarrow 4PH_3$

14 Determine the oxidation numbers of the underlined atom in the following compounds and ions.

- **a** $\underline{Cu}O$
- **b** $\underline{Fe}(OH)_3$
- **c** $H\underline{Cl}O_2$
- **d** $\underline{Mn}O_4^-$
- **e** $\underline{Cr_2}O_7^{2-}$

15 Copper bowls and trays can be decorated by etching patterns on them using concentrated nitric acid. The overall reaction is:

$$Cu(s) + 4HNO_3\ (aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$$

- **a** What is the oxidation number of copper:
  - **i** before the reaction?
  - **ii** after the reaction?
- **b** What is the oxidation number of nitrogen:
  - **i** before the reaction?
  - **ii** after the reaction?
- **c** Name the oxidising agent and reducing agent in this process.

16 Complete the following table, giving the conjugate redox pairs for each of the reactions.

Equation	Conjugate redox pair (oxidation)	Conjugate redox pair (reduction)
$Fe(s) + I_2(aq) \rightarrow FeI_2(aq)$		
$Mg(s) + FeCl_2(aq) \rightarrow MgCl_2(aq) + Fe(s)$		
$10Br^-(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Br_2(aq)$		
$Cu(s) + 2NO_3^-(aq) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$		

More complex redox equations

17 Complete the summary below as you balance the half-equation for the reduction of NO_3^- to NO_2 in acidic solution.

$NO_3^-(aq) \rightarrow NO_2(g)$

Step	Task	How it's done	Half-equation
1	Balance nitrogens.		$NO_3^-(aq) \rightarrow NO_2(g)$
2	Balance oxygens by adding _______.	Add _____ H_2O molecule(s) to the right-hand side of the equation.	
3	Balance hydrogens by adding _______.	Add ______ H^+ ion(s) to _________ of the equation.	
4	Balance charge by adding _______.	Charge on left-hand side = ______ Charge on right-hand side = ______ Add ______ e^- to the _______ of the equation.	
5	Add state symbols to give the final half equation.	Give the appropriate states for each reactant and product in the equation.	

18 The unbalanced half-equation for the reduction of the iodate ion (IO_3^-) is:

$$2IO_3^-(aq) + xH^+(aq) + ye^- \rightarrow I_2(aq) + zH_2O(l)$$

Complete the equation by inserting the correct coefficients for *x*, *y* and *z*. (Hint: You will need to write the relevant half-equations first.)

19 When sulfur dioxide is bubbled through an acidified solution of sodium dichromate, sulfate ions and green chromium(III) ions are formed. Write the half-equations for this reaction and then deduce the balanced overall equation.

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20 In dry cells commonly used to power torches, energy is produced from the reaction of zinc metal with solid MnO_2. During this reaction, Zn^{2+} ions and solid Mn_2O_3 are formed. Write half-equations, and hence an overall equation, for the reaction.

21 Answer the following questions about the reaction of $H_3AsO_4(aq)$ with $I^-(aq)$. The unbalanced equation for the reaction is:

$H_3AsO_4(aq) + I^-(aq) \rightarrow As_2O_3(s) + IO_3^-(aq) + H_2O(l)$

- **a** Write the two half-equations for the reaction.
- **b** Write a balanced overall equation using your two half-equations from part a.

The reactivity series of metals

You may need to refer to the reactivity series of metals to answer Questions 22–27.

22 List the following in order of increasing reducing strength.

Mg, Ag, Ni, Sn, Li, Cu

23 Predict whether the following mixtures would result in spontaneous reactions. Write an overall equation for each reaction that you predict will occur.

- **a** Zinc metal is added to a solution of silver nitrate.
- **b** Copper metal is placed in an aluminium chloride solution.
- **c** Tin(II) sulfate is placed in a copper container.
- **d** Magnesium metal is added to a solution of lead nitrate.
- **e** Silver metal is added to nickel chloride solution.
- **f** Solutions of potassium chloride and copper(II) chloride are mixed.
- **g** Potassium nitrate solution is added to a silver container.
- **h** Elemental lead is placed in a solution of silver nitrate.

24 Would you expect a reaction when a piece of zinc metal is added to solutions of the following compounds? If so, write a fully balanced chemical equation for the reaction.

- **a** $AlCl_3$
- **b** $AgNO_3$
- **c** $SnCl_2$
- **d** $CuSO_4$

25 You are given three colourless solutions (A, B and C) known to be sodium nitrate, silver nitrate and lead(II) nitrate, but not necessarily in this order. You also have some pieces of magnesium ribbon and copper wire. Describe how you could identify each of the solutions using only the chemicals supplied.

26 An unknown metal is placed in solutions of aluminium nitrate and iron(II) sulfate. After a period of time, the metal is found to have reacted with the iron(II) sulfate solution, but not the aluminium nitrate solution. Suggest the name of the unknown metal.

27 Iron nails are placed into solutions of $CuSO_4$, $MgCl_2$, $Pb(NO_3)_2$ and $ZnCl_2$. In which solutions would you expect a coating of another metal to appear on the nail? Explain your answer.

Connecting the main ideas

28 Construct a concept map that shows the links between the following terms:

oxidising agent, reducing agent, electrons, oxidation, reduction

29 As a result of a traffic accident, residents in a Perth suburb had to be evacuated when toxic fumes leaked from a container of sodium dithionite ($Na_2S_2O_4$). The dithionite ion reacts with water according to the equation:

$2S_2O_4^{2-}(aq) + H_2O(l) \rightarrow S_2O_3^{2-}(aq) + 2HSO_3^-(aq)$

- **a** State the oxidation number of the sulfur in the following ions.
  - **i** $S_2O_4^{2-}$
  - **ii** $S_2O_3^{2-}$
  - **iii** HSO_3^-
- **b** Write half-equations for the oxidation and reduction reactions that occur when sodium dithionite is mixed with water.

30 Solid ammonium dichromate decomposes to form chromium(III) oxide, nitrogen gas and steam.

- **a** Calculate the oxidation numbers of chromium and nitrogen in the reactant ammonium dichromate ($(NH_4)_2Cr_2O_7$) and the products Cr_2O_3 and N_2. Identify which reactants have been reduced and oxidised.
- **b** Complete and balance the following half-equations.
  - **i** $NH_4^+(s) \rightarrow N_2(g)$
  - **ii** $Cr_2O_7^{2-}(s) \rightarrow Cr_2O_3(s)$
- **c** Identify each of the half-equations in part b as either reduction or oxidation processes and explain your answer in terms of oxidation numbers.
- **d** Write the balanced overall equation for the reaction that occurs.
- **e** Identify the conjugate redox pairs for the reaction.

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31 The thermite process can be used to weld lengths of railway track together. A mould placed over the ends of the two rails to be joined is filled with a charge of aluminium powder and iron(III) oxide. When the mixture is ignited, a redox reaction occurs to form molten iron, which joins the rails together, and aluminium oxide.

- **a** Write a half-equation for the conversion of iron(III) oxide to metallic iron and oxide ions.
- **b** Is the half-equation you wrote for part **a** an oxidation or a reduction process?
- **c** Write the overall equation for the thermite process.
- **d** What mass of iron(III) oxide must be present in the charge if each joint requires 3.70 g of iron to weld it together?

32 The following equations form part of the reactivity series. They are ranked in the order shown.

$Ag^+(aq) + e^- \rightarrow Ag(s)$
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$

- **a** Which species is the strongest oxidising agent and which is the weakest oxidising agent?
- **b** Which species is the strongest reducing agent and which is the weakest reducing agent?
- **c** Lead rods are placed in solutions of silver nitrate, iron(II) sulfate and magnesium chloride. In which solutions would you expect to see a coating of another metal form on the lead rod? Explain.
- **d** Which of the metals silver, zinc or magnesium might be coated with lead when immersed in a solution of lead(II) nitrate?

33 Consider the following information relating to metals, R, S and T, and solutions of their salts, $Q(NO_3)_2$, RNO_3 and $S(NO_3)_2$.

Three experiments are carried out with these metals to determine their order of reactivity. Equations representing what happened in these experiments are listed below.

Experiment 1: $T(s) + 2RNO_3(aq) \rightarrow T(NO_3)_2(aq) + 2R(s)$
Experiment 2: $T(NO_3)_2(aq) + S(s) \rightarrow$ no reaction
Experiment 3: $S(s) + RNO_3(aq) \rightarrow$ no reaction

Determine the order of reactivity of the three metals, from least reactive to most reactive.

Page Proofs