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7

Oxidation and Reduction

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OBJECTIVES

- Defines oxidation, reduction and redox reaction
- Explains how to work out oxidation numbers and write redox equations
- Shows you how to use standard reduction potentials to decide if reactions can occur
- Discusses corrosion and redox reactions in nature

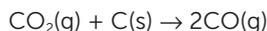
7.1 Redox reactions

A **redox** reaction is an important type of chemical reaction. In such a reaction, one reactant is **oxidized** and another reactant is **reduced**.

Definitions of oxidation and reduction

Oxidation was once regarded as a chemical reaction in which oxygen was added to a substance, whereas reduction occurred when oxygen was lost.

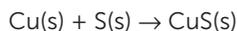
For example, in the reaction



carbon is oxidized to carbon monoxide (an atom of carbon gains an oxygen atom), while carbon dioxide is reduced to carbon monoxide (a molecule of carbon dioxide loses an atom of oxygen).

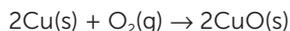
The definition was later broadened to include hydrogen: oxidation was removal of hydrogen from a substance, while reduction took place when hydrogen was added.

These definitions, however, do not help when oxygen and hydrogen are not involved. Consider a reaction such as



Oxygen and sulfur both have six electrons in the outer shell of their atoms and their reactions tend to be very similar. It is reasonable to expect that copper undergoes much the same process here, as it does when it reacts with oxygen.

When copper reacts with oxygen (**is oxidized**) to form copper(II) oxide, the chemical equation may be written as



In this reaction, a copper atom loses two electrons:



Each oxygen atom in an oxygen molecule gains two electrons from the copper atom (**the oxygen is reduced**):

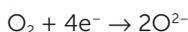


Or, since oxygen gas reacts with copper,



The overall equation can be obtained by adding the two 'half-reactions' together, so that the electrons cancel out on each side:

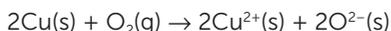
- 1 First multiply the equation for the oxidation of copper by two, so that this half-reaction contains the same number of electrons as the half-equation for the reduction of O_2 :



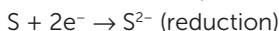
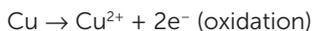
- 2 Then add the two half-reactions, and the number of electrons on each side cancels out:



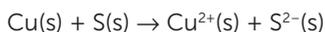
- 3 The overall equation is



Similar equations can be written for the reaction of copper with sulfur:



Adding and cancelling electrons gives



Here, a copper atom loses two electrons just as it did in the reaction with oxygen – **it is oxidized**. Sulfur gains two electrons and **is reduced**.

Reactions such as these led to a far more general definition of the terms 'oxidation' and 'reduction':

Oxidation occurs when electrons are lost, reduction occurs when electrons are gained.

To help you remember:

OILRIG

Oxidation **i**s electron **l**oss; **r**eduction **i**s electron **g**ain

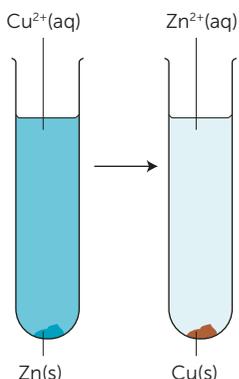


Fig. 7.1 Reaction of zinc with copper(II) sulfate solution.

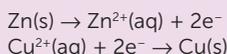
EXERCISE 7A

The reaction of zinc with aqueous copper(II) sulfate

When solid zinc is added to blue copper(II) sulfate solution, the solution gradually becomes paler and a red-brown solid (copper) is deposited at the bottom of the test-tube. This is shown in Fig. 7.1.

In this reaction, the zinc metal supplies two electrons to the copper ions and copper is precipitated.

The two half-reactions are:



- Which half-reaction represents reduction?
- Which half-reaction represents oxidation?
- Write the overall redox equation for the reaction.
- The sulfate ions are not included in the redox equation. Why?

EXERCISE 7B

Oxidation and reduction

In the following reactions, which substances are oxidized and which are reduced?

- $2\text{Zn(s)} + \text{O}_2(\text{g}) \rightarrow 2\text{ZnO(s)}$
- $\text{Mg(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Mg}^{2+}(\text{aq}) + \text{Cu(s)}$
- $\text{Cl}_2(\text{g}) + 2\text{I}^{-}(\text{aq}) \rightarrow 2\text{Cl}^{-}(\text{aq}) + \text{I}_2(\text{aq})$
- $2\text{Na(s)} + \text{Cl}_2(\text{g}) \rightarrow 2\text{NaCl(s)}$
- $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl(g)}$

7.2 Oxidation numbers

The **oxidation number** or **oxidation state** of an atom is a positive or negative number which is decided using agreed rules (see Box 7.1). Oxidation numbers are used to widen the definition of oxidation and reduction, with **oxidation being defined as an increase in oxidation number and reduction as a decrease in oxidation number**.

Note that the oxidation number system is just designed to help you work out whether substances are oxidized or reduced. *It does not tell you anything about the bonding in a compound.* For example, the fact that carbon has an oxidation number of +4 in some of its compounds does *not* mean that it exists as +4 ions in these compounds.

BOX 7.1

Oxidation numbers

The following elements nearly always have the same oxidation number in their compounds. They are used as 'standards' to help assign the oxidation numbers of other elements.

There are important exceptions to the elements marked with an asterisk (*), but they will not be dealt with here. Different oxidation numbers of Cl and O will be dealt with at a later stage in the unit.

Element number	Oxidation number
$\text{K}^+ \text{Na}^+$	+1
$\text{Mg}^{2+} \text{Ca}^{2+}$	+2
Al^{3+}	+3
H^+ (or covalent H)*	+1
F^- (or covalent F)	-1
Cl^- (or covalent Cl)*	-1
O^{2-} (or covalent O)*	-2

Rules for working out oxidation numbers

- The oxidation number of an atom of a *free element* is zero. For example, the oxidation number of nitrogen in N_2 or calcium in Ca is 0.
- The oxidation number of the ion of an element is equal to its charge. For example, the oxidation number of copper in Cu^{2+} is +2 and the oxidation number of oxygen in O^{2-} is -2.
- The *algebraic sum* of the oxidation numbers of the atoms in the formula of an electrically neutral compound is zero. For $Ca(OH)_2$, for example, the sum of the oxidation numbers is

$$[+2 \text{ for Ca}] + [2(-2) \text{ for O}] + [2(+1) \text{ for H}] = 0$$
- For convenience, shared electrons in covalent compounds are assigned to the element having the greater electronegativity. For example, the oxidation number for phosphorus in PCl_3 is +3 (chlorine is -1), since phosphorus is less electronegative than chlorine.
- The *algebraic sum* of the oxidation numbers of all the atoms of an ion is equal to the charge on the ion. In SO_4^{2-} , for example, the sum of the oxidation numbers is

$$[+6 \text{ for S}] + [4(-2) \text{ for O}] = -2$$

Remember that:

during chemical reactions an increase in oxidation number signifies **OXIDATION**; a decrease, **REDUCTION**.

EXERCISE 7C

Assigning oxidation numbers

Assign oxidation numbers to the underlined atoms in the following examples:

- S O_2
- N H_3
- S $_8$
- Cr Cl_3
- N O_3^-
- Mn O_4^-
- Xe F_2
- Ca(V O_3) $_2$
- Bi O_3^-
- Cr $_2O_7^{2-}$

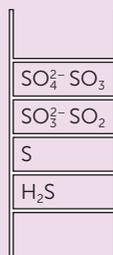
EXERCISE 7D

Oxidation ladders

Some elements have many oxidation states. You can construct redox 'ladders' like the one shown below for sulfur:

- What is the oxidation state of sulfur on each rung of the 'ladder'?
- SO_2 reacts with water to form the *sulfite* ion SO_3^{2-} . Is this a redox reaction?
- H_2S reacts with SO_2 to precipitate sulfur:

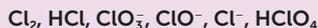
$$2H_2S(g) + SO_2(g) \rightarrow 2H_2O(l) + 3S(s)$$
 Which species is reduced? Which species is oxidized?



EXERCISE 7E

Redox ladder for chlorine

Chlorine can have different oxidation states. Using the following species, construct a redox ladder for chlorine:



Note that those species with the lowest oxidation number for chlorine should be at the bottom of the ladder, whereas those with the highest oxidation number for chlorine are at the top.

EXERCISE 7F

Oxidizing and reducing agents

Look back at the redox ladder for sulfur in Exercise 7D:

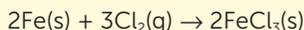
- (i) Which sulfur species can act as both reducing and oxidizing agents in different chemical reactions?
- (ii) Which sulfur species can only act as oxidizing agents and why?
- (iii) Which sulfur species can only act as reducing agents and why?

7.3 Oxidizing and reducing agents

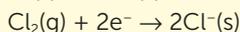
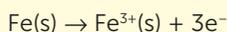
An **oxidizing agent** is a substance that takes up electrons during a chemical reaction and, in doing so, becomes **reduced**. A **reducing agent** supplies the electrons in this process and so becomes **oxidized**.

EXAMPLE 7.1

When iron is heated in chlorine gas, iron(III) chloride is produced. The 'ordinary' equation is:



The redox half-equations are



Here, iron is acting as a *reducing agent* because it supplies electrons to chlorine and is *oxidized*.

Chlorine is acting as an *oxidizing agent* because it accepts electrons from iron and is *reduced*.

7.4 Writing and balancing redox equations

In order to write a redox equation, it is first necessary to write the two half-reactions that identify the oxidation and reduction processes taking place. The overall redox equation is then obtained by adding these two half-reactions together, so that the electrons in each half-reaction cancel out.

To write the half-reactions, follow these simple rules:

- 1 Identify the atoms that are oxidized and reduced, using the oxidation number method.

Most of the reactions that you will come across at this stage, will occur in neutral or acid solution, and step 2 applies.

- 2 Balance the half-reactions:
 - (i) Make sure that there are the same number of atoms of the element that is oxidized (or reduced) on each side of the half-reaction.
 - (ii) If there are any oxygen atoms present, balance them by adding water molecules to the other side of the half-reaction.
 - (iii) If there are hydrogen atoms present, balance them by adding hydrogen ions on the other side of the half-reaction.
 - (iv) Make sure that the half-reactions have the same overall charge on each side by adding electrons.

Note that the rules are slightly different if the reaction occurs in basic solution: hydrogen atoms are balanced using H_2O molecules and then the same number of OH^- ions are added to the opposite side of the equation to balance the oxygens. Carry on as before, adding electrons to balance the charges.

EXAMPLE 7.2

Write the overall redox equation for the oxidation of iron(II) ions to iron(III) ions by the manganate(VII) or permanganate ion, MnO_4^- , in acid solution. The manganate(VII) ion reacts to form the manganese(II) ion, Mn^{2+} .

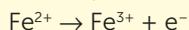
Answer
The oxidation half-reaction

The question tells you that iron(II) is oxidized, but you can check on this by working out the oxidation numbers of iron before and after the reaction:



therefore, an increase in oxidation number, i.e. oxidation, has occurred.

There are the same number of atoms on each side of this half-reaction, and no oxygen or hydrogen atoms, so all that remains to be done is to make sure that the overall charge is the same on each side of the half-equation. By adding one electron to the right-hand side, the overall charge on each side of the equation becomes +2 (*think of an electron as a unit negative charge, which will cancel out a positive charge*):



The half-equation above represents the oxidation reaction.

The reduction half-reaction

The manganate(VII) ion reacts to form manganese(II). Check that this is a reduction by working out the oxidation numbers of manganese before and after the reaction:



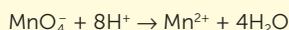
therefore, a decrease in oxidation number, i.e. reduction, has occurred.

There are the same number of manganese atoms on each side of the half-reaction, but the oxygen atoms need to be balanced:

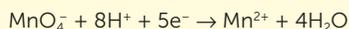
- 1 Balance the oxygens with water molecules:



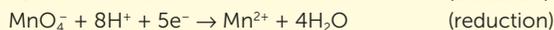
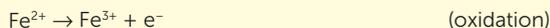
- 2 Now H atoms have been introduced, so they need to be balanced with H^+ ions:



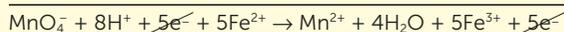
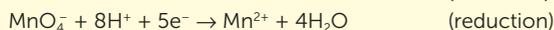
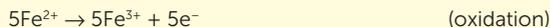
- 3 Balance the charges on each side of the half-reaction by adding electrons:



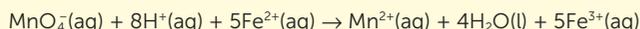
Each side of the equation now has an overall charge of +2. The above equation represents the reduction reaction. To construct the overall redox equation, the two half-reactions must be added together so that the electrons cancel out:



The first half-reaction must be multiplied by five, then the equations added together:



The overall redox equation is therefore



EXERCISE 7G

Writing and balancing redox equations

1 Write half-equations for:

- (i) the oxidation of I^- to IO_3^-
- (ii) the reduction of NO_3^- to NO in acidic solution
- (iii) the reduction of $Cr_2O_7^{2-}$ to Cr^{3+} in acidic solution
- (iv) the reduction of H_2O_2 to H_2O in acidic solution
- (v) the oxidation of S^{2-} to SO_4^{2-} in *basic* solution.

2 Write an overall redox equation for:

- (i) The reaction of copper with silver nitrate, in aqueous solution, to produce copper(II) nitrate and silver.
- (ii) The oxidation of copper metal to copper(II) nitrate by concentrated nitric acid (*regard the reduction of nitric acid as the ion NO_3^- being reduced to brown NO_2 gas.*)
- (iii) The reduction of I_2 by thiosulfate, $S_2O_3^{2-}$, to I^- in aqueous solution. Thiosulfate is oxidized to tetrathionate, $S_4O_6^{2-}$.
- (iv) The oxidation of I^- to I_2 by H_2O_2 in acid solution (H_2O_2 is reduced to H_2O). (Note that in H_2O_2 , the oxidation number of oxygen is -1 .)
- (v) The oxidation of H_2O_2 to O_2 by ClO_2^- (ClO_2^- is reduced to Cl^-).

BOX 7.2

The breathalyser

The first type of breathalyser was a disposable device consisting of a plastic tube packed with yellow crystals. The person was required to blow through the tube into a 1 dm^3 plastic bag for about 15 s. Alcohol vapour in the subject's breath reacted with the yellow crystals and turned them green. If the green stain extended

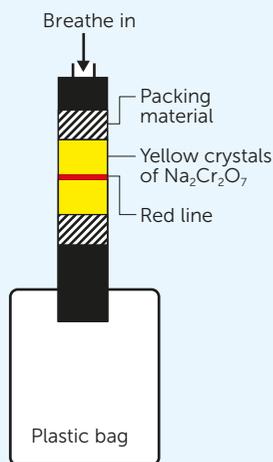
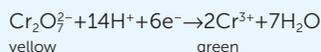


Fig. 7.2 The Alcolyser* breathalyser.

beyond the red line drawn on the tube, then the subject had failed the test (Fig. 7.2).

The yellow crystals are sodium dichromate, $Na_2Cr_2O_7$, and the redox reaction taking place is the reduction of the dichromate(VI) ion, $Cr_2O_7^{2-}$, to the green Cr^{3+} ion, by alcohol, under *acidic* conditions:



Many police forces now use an Alcometer* instead of the disposable dichromate tubes. The Alcometer is a small instrument with disposable mouthpiece tubes. The subject blows into the instrument and their alcohol level can be read from a digital display. The instrument is an electrochemical cell known as a fuel cell which generates a voltage in proportion to the alcohol vapour concentration in the breath.

If a person is 'over the limit' for either of these roadside tests, they are taken to the police station, where a second instrument (a simple infrared

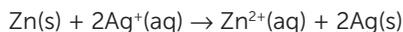
spectrometer (see Unit 20)) is used to measure accurately the alcohol concentration.



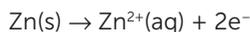
*Trademarks of Lion Laboratories Ltd, Ty Verlon Industrial Estate, Barry, South Wales.

7-5 Redox couples

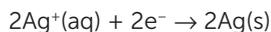
Think of a piece of zinc metal, Zn(s) , dipped in a solution of silver ions, $\text{Ag}^+(\text{aq})$. A reaction is seen to occur, and solid silver is produced:



The half-reactions that make up this overall reaction are:



and



The fact that there is a reaction between Zn(s) and $\text{Ag}^+(\text{aq})$ suggests that the silver ions want to accept electrons more than the zinc atoms want to keep them.

No reaction takes place when zinc metal is added to magnesium ions, $\text{Mg}^{2+}(\text{aq})$. This suggests that magnesium ions in solution have a smaller tendency to accept electrons, and form Mg(s) , than do silver ions, forming Ag(s) .

The pairs of species involved here, $\text{Ag}^+(\text{aq})/\text{Ag(s)}$ and $\text{Mg}^{2+}(\text{aq})/\text{Mg(s)}$ are known as **redox couples**. Therefore, our experiments suggest that the $\text{Ag}^+(\text{aq})/\text{Ag(s)}$ redox couple is a *stronger oxidizing agent* than the $\text{Mg}^{2+}(\text{aq})/\text{Mg(s)}$ redox couple. Since a strong oxidizing agent may be described as a weak reducing agent, we could also say that the $\text{Mg}^{2+}(\text{aq})/\text{Mg(s)}$ redox couple is a *stronger reducing agent* than the $\text{Ag}^+(\text{aq})/\text{Ag(s)}$ redox couple.

The relative oxidizing or reducing strengths of redox couples are expressed in terms of their **standard electrode potentials**, E^\ominus , which have the units of volts. It is impossible to measure the standard electrode potentials of redox couples in isolation, without introducing other metals into the electrical circuit. In practice, the redox couple under study is connected to a **reference redox couple** in an **electrochemical cell**. Voltage measurements then give a relative potential difference. The reference redox couple used is $\text{H}^+(\text{aq})/\text{H}_2(\text{g})$, which (under agreed standard conditions) is given an E^\ominus value of zero.

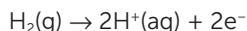
The standard hydrogen electrode (SHE)

Experimentally, the $\text{H}^+(\text{aq})/\text{H}_2(\text{g})$ couple is arranged in the form of a **hydrogen electrode**. A hydrogen electrode is made up of a piece of platinum foil, coated with fine particles of platinum, dipped into a solution of hydrogen ions, with hydrogen gas bubbling over the surface of the platinum (Fig. 7.3).

The platinum provides a surface upon which either of the following reactions may occur:



or



These two possibilities are summarized by the equation



or it could also be written as

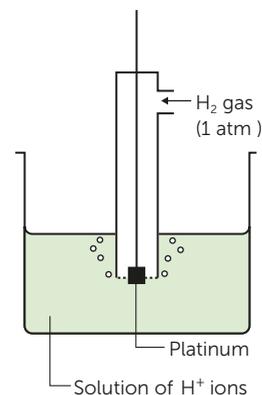


Fig. 7.3 The standard hydrogen electrode.



Photograph of a standard hydrogen electrode

The **standard hydrogen electrode** (SHE; Fig. 7.3) is a hydrogen electrode where $\text{H}^+(\text{aq})$ and $\text{H}_2(\text{g})$ are in their **standard states** (see page 217). This means that the concentration of $\text{H}^+(\text{aq})$ is 1 mol dm^{-3} , and the hydrogen gas is at a pressure of 1 atm. By agreement, the potential difference between the $\text{H}^+(\text{aq})$ solution and the Pt electrode in the SHE is set to zero at all temperatures. This is written as:

$$E^\ominus(\text{H}^+(\text{aq}), \text{H}_2(\text{g})) = 0$$

where the use of the symbol \ominus shows that the substances are in their standard states.

Other standard electrodes

The electrode of the $\text{Ag}^+(\text{aq})/\text{Ag}(\text{s})$ redox couple consists of a rod of silver dipped in a solution of silver ions. The $\text{Ag}^+(\text{aq})/\text{Ag}(\text{s})$ electrode becomes the **standard** $\text{Ag}^+(\text{aq})/\text{Ag}(\text{s})$ electrode if the silver is pure, and the silver ion concentration is 1 mol dm^{-3} .

The electrode of the $\text{Fe}^{3+}(\text{aq})/\text{Fe}^{2+}(\text{aq})$ redox couple has a different construction. It consists of a piece of platinum dipped in a mixture of both ions. In an electrochemical cell, the Pt connects the electrode to the rest of the cell. The Pt also provides a surface upon which electrode reactions may occur. The **standard** $\text{Fe}^{3+}(\text{aq})/\text{Fe}^{2+}(\text{aq})$ electrode contains both ions at a concentration of 1 mol dm^{-3} .

Measuring E^\ominus values by making an electrochemical cell

1 Measuring $E^\ominus(\text{Ag}^+(\text{aq})/\text{Ag}(\text{s}))$

We will now see how the standard electrode potential of a redox couple may be found by experiment. Figure 7.4 shows the electrochemical cell composed of the standard hydrogen and standard silver ion/silver electrodes. All measurements are made at 25°C . The two electrodes are connected by:

- 1 a wire through which electrons can pass;

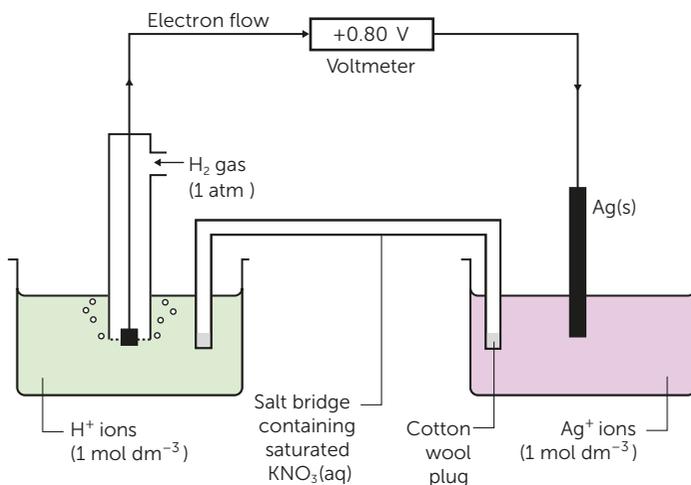


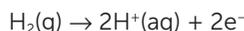
Fig. 7.4 Electrochemical cell used in the determination of $E^\ominus(\text{Ag}^+(\text{aq})/\text{Ag}(\text{s}))$.

2 a **salt bridge** (a glass tube that contains a saturated solution of an ionic salt, such as KNO_3) which completes the electrical circuit.

If we measure the voltage of the cell (the **cell potential**) using a high-resistance voltmeter, we will not be using up any electrical current produced by the cell, and very little chemical reaction takes place. Under these conditions, the measured voltage does not fall during the measurement.

Which electrode is connected to the positive terminal of the voltmeter? By trial and error, it is found that only if the $\text{Ag}^+(\text{aq})/\text{Ag}(\text{s})$ electrode is connected to the positive terminal is the cell potential **positive**. (A voltage of $+0.80\text{ V}$ is actually obtained; if the connections were reversed, the voltage reading would be -0.80 V .) Because of this, the $\text{Ag}^+(\text{aq})/\text{Ag}(\text{s})$ electrode is said to be the cell **cathode** (+) and the hydrogen electrode the cell **anode** (-).

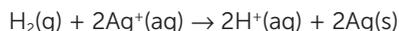
Electrons flow from the anode to the cathode. This means that the hydrogen electrode is losing electrons (oxidation); this is only possible if the $\text{H}^+(\text{aq})/\text{H}_2(\text{g})$ redox couple is undergoing the reaction:



The electrons then pass through the circuit and move to the cathode where they cause the $\text{Ag}^+(\text{aq})/\text{Ag}(\text{s})$ redox couple to be reduced within the $\text{Ag}^+(\text{aq})/\text{Ag}(\text{s})$ electrode:

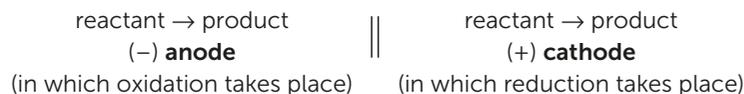


The overall cell reaction is:

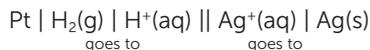


(The same reaction occurs outside a cell, if hydrogen gas is bubbled into a solution containing silver ions. However, in that case heat – not electricity – is made.)

The **cell diagram** for any electrochemical cell follows the pattern:



where $||$ symbolizes the salt bridge. In our case:



which shows that $\text{H}_2(\text{g})$ is oxidized to $\text{H}^+(\text{aq})$ (the product at the anode), while $\text{Ag}^+(\text{aq})$ is reduced to $\text{Ag}(\text{s})$ (the product at the cathode).

The standard potential of the cell, $E^\ominus = +0.80\text{ V}$, is related to the standard electrode potentials for each redox couple by the following equation:

$$E^\ominus = E_{\text{R}}^\ominus - E_{\text{L}}^\ominus$$

which applies to all cells, and in which E_{R}^\ominus is the standard electrode potential of the right-hand electrode (cathode) and E_{L}^\ominus the standard electrode potential of the left-hand electrode (anode) as they appear in the cell diagram. Here, $E_{\text{R}}^\ominus = E^\ominus(\text{Ag}^+(\text{aq})/\text{Ag}(\text{s}))$ and $E_{\text{L}}^\ominus = E^\ominus(\text{H}^+(\text{aq}), \text{H}_2(\text{g})) = 0$ (by definition). Thus:

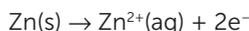
$$+0.80\text{ V} = E^\ominus(\text{Ag}^+(\text{aq})/\text{Ag}(\text{s})) - 0$$

and $E^\ominus(\text{Ag}^+(\text{aq})/\text{Ag}(\text{s})) = +0.80\text{ V}$.

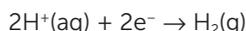
2 Finding $E^\ominus(\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s}))$

Suppose we wanted to measure $E^\ominus(\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s}))$. Our first step is to set up the electrochemical cell, consisting of the SHE and standard $(\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s}))$ electrode (consisting of pure Zn metal dipped into $1 \text{ mol dm}^{-3} \text{ Zn}^{2+}(\text{aq})$) connected by a salt bridge.

If the standard $\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s})$ electrode is connected to the negative pole of the voltmeter, the voltage reading is found to be $+0.76 \text{ V}$. The positive voltage shows that the $\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s})$ electrode is the anode. At the anode, the $\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s})$ redox couple undergoes oxidation:



The electrons cause the $\text{H}^+(\text{aq})/\text{H}_2(\text{g})$ redox couple to be reduced within the cathode of the SHE:



The overall cell reaction is



The cell diagram is



The cell potential is $+0.76 \text{ V}$:

$$\begin{aligned} E^\ominus &= E^\ominus_{\text{R}} - E^\ominus_{\text{L}} \\ 0.76 &= E^\ominus(\text{H}^+(\text{aq}), \text{H}_2(\text{g})) - E^\ominus(\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s})) \\ 0.76 &= 0 - E^\ominus(\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s})) \end{aligned}$$

or,

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

We have now looked at two electrochemical cells. In the first, where the E^\ominus of the redox couple under investigation proved to be positive, the $\text{H}^+(\text{aq})/\text{H}_2(\text{g})$ couple undergoes oxidation (Fig. 7.5(a)). In the second, where the E^\ominus of the redox couple under investigation proved to be negative, the $\text{H}^+(\text{aq})/\text{H}_2(\text{g})$ couple undergoes reduction (Fig. 7.5(b)). Generalizing:

- 1 A negative E^\ominus means that a redox couple is a stronger reducing agent than the $\text{H}^+(\text{aq})/\text{H}_2(\text{g})$ couple.
- 2 A positive E^\ominus means that a redox couple is a weaker reducing agent than the $\text{H}^+(\text{aq})/\text{H}_2(\text{g})$ couple.

The reverse statements apply to the oxidizing power of these redox couples.

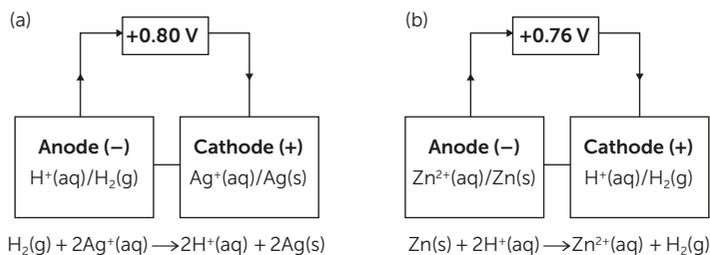


Fig. 7.5 The flow of electrons in cells involving the SHE in which (a) $\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s})$, and (b) $\text{Ag}^+(\text{aq})/\text{Ag}(\text{s})$ form the other electrode.

Table 7.1 Standard electrode potentials

	Redox couple	Reaction equation when redox couple is reduced	E^\ominus at 25°C/V
Strong Oxidizing Agents	$F_2(g)/F^-(aq)$	$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	+2.87
	$Cl_2(g)/Cl^-(aq)$	$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	+1.36
	$Br_2(l)/Br^-(aq)$	$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$	+1.09
	$Ag^+(aq)/Ag(s)$	$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.80
	$Fe^{3+}(aq)/Fe^{2+}(aq)$	$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	+0.77
	$I_2(s)/I^-(aq)$	$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	+0.54
	$Cu^{2+}(aq)/Cu(s)$	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	+0.34
	$H^+(aq)/H_2(g)$	$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0 (by definition)
	$Fe^{2+}(aq)/Fe(s)$	$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	-0.44
	$Cr^{3+}(aq)/Cr(s)$	$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	-0.74
Strong Reducing Agents	$Zn^{2+}(aq)/Zn(s)$	$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.76
	$Mg^{2+}(aq)/Mg(s)$	$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	-2.37
	$Na^+(aq)/Na(s)$	$Na^+(aq) + e^- \rightarrow Na(s)$	-2.71

Key points about the standard electrode potentials of redox couples

- E^\ominus values are also known as **standard reduction potentials**. Table 7.1 shows selected E^\ominus values which were measured at 25°C. Note that the redox couples are listed with the oxidized species first (e.g. $Na^+(aq)/Na(s)$, not $Na(s)/Na^+(aq)$).
- Measurements of E^\ominus may be carried out at other temperatures. E^\ominus values do vary with temperature, apart from E^\ominus ($H^+(aq)/H_2$), which by agreement is set to zero at all temperatures.
- Some E^\ominus values, such as $E^\ominus(Na^+(aq)/Na(s))$, cannot be found using simple electrochemical cells, and are calculated from other data.
- Strictly speaking, E^\ominus values apply to couples, and not to single species. For example, we cannot speak of $E^\ominus(Na)$. The fact that $E^\ominus(Na^+(aq)/Na(s)) = -2.71$ V, shows specifically that sodium has a strong tendency to form Na^+ ions in solution (and not to form, say, Na^-).
- E^\ominus values may be used to predict whether or not redox reactions are allowed to occur. (Using the language of Unit 15, we would say that a reaction that is allowed to occur has a large value for the equilibrium constant K_c .) This is discussed in the next section, but note that E^\ominus values do not permit any predictions to be made about the rate of a reaction.

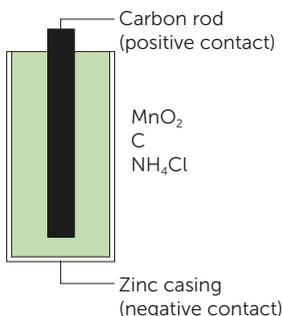
BOX 7.3

Dry cells

The trouble with 'wet' cells is that the solutions (*the electrolyte*) might leak out. In the dry cell, the electrolyte is a damp paste. This type of cell is used in torches, walkmans and clocks. Many dry cells use the reactions of zinc and manganese(IV) oxide:



Other reactions occur, but we will not discuss them here. A diagram of a dry cell is shown in Fig. 7.6.


Fig. 7.6 A dry cell.

EXERCISE 7H

Electrochemical cells and E^\ominus

A cell, consisting of the SHE (as anode) and the standard $Cu^{2+}(aq)/Cu(s)$ electrode, gives a standard cell potential of +0.34 V at 25°C.

- Write down the cell diagram.
- Calculate $E^\ominus(Cu^{2+}(aq)/Cu(s))$.
- Write down the overall reaction that occurs in the cell.

Predicting whether reactions can occur

Standard electrode potentials (E^\ominus values) may be used to decide whether redox reactions are allowed to occur. The key point to remember here is that the half-reaction having the more positive electrode potential occurs as a reduction, while the half-reaction having the more negative electrode potential occurs as an oxidation.

To help you apply this easily:

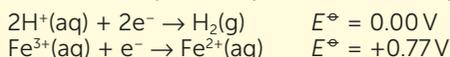
Write down both half-reactions, with the half-reaction possessing the *more negative* (or *least positive*) E^\ominus value at the top. Then draw *anticlockwise arrows* to predict whether the overall reaction can occur.

EXAMPLE 7.3

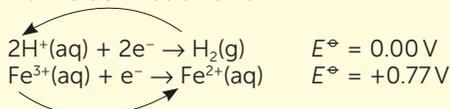
Will hydrogen gas reduce $\text{Fe}^{3+}(\text{aq})$ to $\text{Fe}^{2+}(\text{aq})$?

Answer

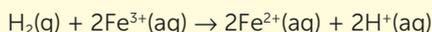
Write down both half-reactions, with the half-reaction possessing the more negative (or least positive) potential at the top:



Draw anticlockwise arrows:



The direction in which the arrows point shows that H_2 changes to H^+ and that Fe^{3+} changes to Fe^{2+} . The predicted overall reaction is therefore:



Comments

The conclusion that we can draw from this is that hydrogen gas is capable of reducing $\text{Fe}^{3+}(\text{aq})$ to $\text{Fe}^{2+}(\text{aq})$ at room temperature.

Note, however, *that we cannot predict how fast (or slow!) the reaction will be*. The reaction may be so slow that nothing will appear to happen.

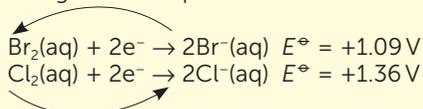
In addition, our predictions only apply to solutions, since E^\ominus values cannot be obtained for dry gases or solids.

EXAMPLE 7.4

Will bromine water ($\text{Br}_2(\text{aq})$) react with an aqueous solution of potassium chloride ($\text{Cl}^-(\text{aq})$)?

Answer

Following the same procedure as above:



In this case, the direction of the arrows shows that $\text{Br}_2(\text{aq})$ and $\text{Cl}^-(\text{aq})$ *stay as they are*. The conclusion is that *there is no reaction* at room temperature.

EXERCISE 71

Predicting reactions

Using the standard reduction potentials in Table 7.1, determine whether the following reactions may occur:

- (i) $\text{Br}_2(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + 2\text{Br}^-(\text{aq})$ (iii) $\text{Zn}(\text{s}) + 2\text{Fe}^{3+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Fe}^{2+}(\text{aq})$
 (ii) $\text{Cu}(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{H}_2(\text{g})$ (iv) $2\text{Fe}^{3+}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{Fe}^{2+}(\text{aq}) + \text{I}_2(\text{aq})$.

7.6 Activity series of metals

The more negative the standard electrode potential, E^\ominus , of a redox couple $\text{M}^{n+}(\text{aq})/\text{M}(\text{s})$, the more powerful a reducing agent is that metal. This means it is a more reactive metal because it loses electrons more easily. We can arrange the metals in order of reducing power, producing an **activity series** of metals (Table 7.2). The metals at the top of the series are more reactive than those below.

A metal in solution can react with a metal ion that appears below it in the table. Hydrogen is included so that the reactivity of metals with aqueous acids may be worked out; when a metal above hydrogen is added to an acidic solution, a reaction will occur and hydrogen gas is given off.

Never mix strongly reducing metals, such as potassium, with acid solutions – the reactions are extremely violent.

Table 7.2 The activity series of metals

Reduction half-reaction	$E^\ominus (\text{M}^{n+}(\text{aq})/\text{M}(\text{s}))/\text{V}$
$\text{K}^+(\text{aq}) + \text{e}^- \rightarrow \text{K}(\text{s})$	-2.92
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ca}(\text{s})$	-2.87
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.71
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$	-2.37
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Al}(\text{s})$	-1.67
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.44
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.25
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}(\text{s})$	-0.14
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$	-0.13
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.34
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	+0.80
$\text{Au}^+(\text{aq}) + \text{e}^- \rightarrow \text{Au}(\text{s})$	+1.68

EXERCISE 73

Activity series of metals

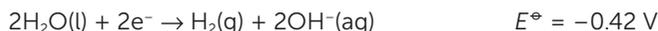
Write redox equations for any reactions that might occur when the following substances are mixed:

- (i) magnesium and silver nitrate solution (iii) nickel and copper(II) sulfate solution (v) copper and dilute sulfuric acid ($\text{H}^+(\text{aq})$).
 (ii) copper and lead(II) nitrate solution (iv) zinc and dilute hydrochloric acid ($\text{H}^+(\text{aq})$)

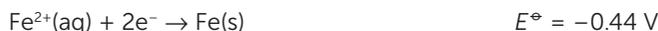
7.7 Corrosion of iron

Rusting

Many metals, including iron, react with air and/or water (**corrode**). The reactivity of metals with air or water can be predicted using reduction potentials. For a neutral solution:



In the case of iron:



Therefore pure water has only a slight tendency to oxidize Fe(s) to Fe²⁺(aq).

However, if oxygen is present, the following half-reaction can occur in neutral solution (pH = 7; see page 151)



Check, by using anticlockwise arrows, that this couple can oxidize Fe to Fe²⁺ and then from Fe²⁺ to Fe³⁺.

Both oxygen and water can therefore oxidize Fe to Fe²⁺ and oxygen is further capable of oxidizing Fe²⁺ to Fe³⁺. These reactions are known as **rusting**.

Rust is a brown, insoluble compound of formula Fe₂O₃·xH₂O (the *x* in the formula indicates that it has a variable composition) which is formed when iron reacts with air and water. Rusting requires the presence of oxygen, water and ionic substances dissolved in the water (**electrolytes**). In the absence of any one of these, little rusting will occur.

EXERCISE 7K

Rusting

- (i) Explain why iron nails do not rust if they are placed in a sealed tube containing boiled water.
- (ii) Why do cars that are kept by the sea rust more rapidly?
- (iii) Rusting occurs much more quickly in areas that are polluted. Can you give a reason for this?

Rust prevention

The following methods may be adopted in order to prevent corrosion of iron or steel:

- 1 Protection of the surface of the metal from air and water by painting, oiling, greasing or coating with a plastic.
- 2 Coat the metal with a more reactive metal (one with a more negative value for E^\ominus) so that, even if the coating is scratched, the more reactive metal will lose electrons in preference to the metal that has been coated. Zinc is often used to coat metals such as iron; this is achieved by dipping the iron in molten zinc, or by **electroplating** the iron. Zinc exposed to the air becomes covered with a film of

zinc oxide, which protects it from further corrosion – the zinc becomes **passive**. Covering a metal with a zinc layer is known as **galvanizing**.

- 3 It is not practical to galvanize large objects, such as ships or pipes. Instead a block of a reactive metal, such as magnesium (or zinc), is attached to the large object and, again, preferentially loses electrons to oxygen. This method of protecting the metal is known as **sacrificial protection**.

7.8 Redox reactions in nature

Nitrogen fixation

Living organisms need nitrogen to make proteins, the ‘building bricks’ of plants and animals. Although nitrogen gas is abundant, making up approximately four-fifths of the atmosphere, most living organisms cannot obtain it directly from the air because it is an unreactive gas. Nitrogen becomes available to plants and animals via the **nitrogen cycle** (Fig. 7.7).

Atmospheric nitrogen is particularly unreactive; however, it is oxidized to NO when lightning flashes. Oxygen in the atmosphere oxidizes NO to NO₂, which reacts with rain water to form the acids HNO₂ and HNO₃. These acids react with metal oxides and carbonates in the soil, to form nitrate and nitrite salts.

Plants obtain nitrogen in the form of nitrate and ammonium ions. Nitrates are very soluble in water and reach the roots of plants easily; the nitrate ion is then taken up and reduced to ammonia by the plant. Nitrogen-fixing bacteria that live in the soil, or in **nodules** on the roots of plants, convert (i.e. **biologically fix**) atmospheric nitrogen into ammonium salts. Animals eat plants and, when both of these organisms die, their organic matter eventually decays into ammonium compounds. Nitrifying and denitrifying bacteria convert ammonium compounds into NO₃⁻ and NO₂⁻, then N₂O and N₂. In this way nitrogen is returned to the atmosphere and the cycle is complete.

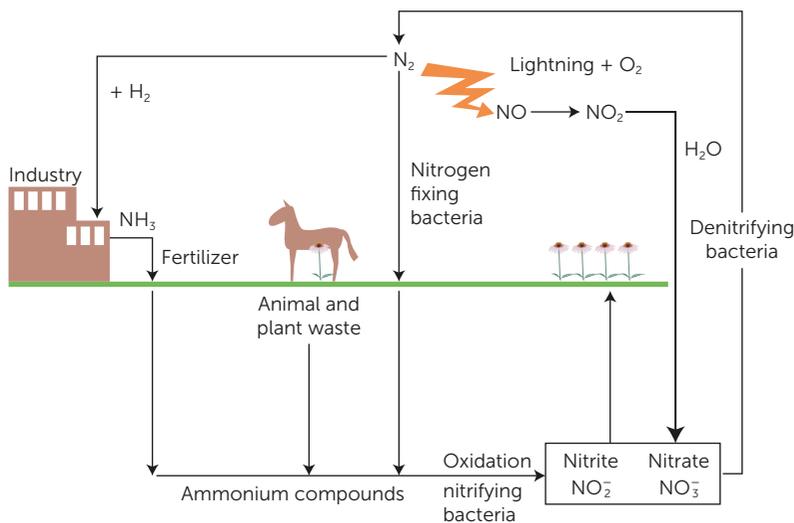


Fig. 7.7 The nitrogen cycle.

EXERCISE 7L

Tinning

Steel food cans coated with tin used to be common. Unfortunately, when damaged they corrode more rapidly than if the coating was not present – explain this phenomenon.

BOX 7.4

Another test for nitrates

If a substance is suspected to contain a nitrate ion (NO_3^-), the presence of the ion can be detected by heating the nitrate with sodium hydroxide solution and **Devarda's alloy**. Devarda's alloy is a roughly equal mixture of aluminium and copper, to which a little zinc is added. If a nitrate is present it is reduced and ammonia is evolved. Ammonia can be detected by its choking smell or, because it is an alkaline gas, it turns damp red litmus paper blue. The detection of ammonia confirms that a nitrate was present.

One redox equation for the reaction is



See also the brown ring test on page 89.

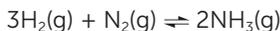
EXERCISE 7M

Nitrogen cycle

Work out the oxidation numbers of all the nitrogen-containing species in the previous section. Construct an 'oxidation state' ladder for nitrogen, using these species.

The availability of nitrogen to plants (and therefore to animals) is vital for producing food. This is why *fertilizers*, ammonium and nitrate salts, are produced industrially to help supply nitrogen to crops.

The **Haber–Bosch process** is an industrial process whereby nitrogen gas is reduced to ammonia using an iron catalyst, and is the first step in the production of fertilizers:



This is a very expensive process, requiring high temperatures and pressures, and the expense is one of the reasons why Third World countries find difficulty in feeding their populations. Biological nitrogen fixation, however, requires only solar energy as its power source and chemists are currently trying to find catalysts that can act in the same way as nitrogen-fixing bacteria.

Electron transport in living systems

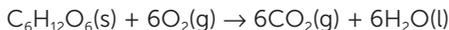
Both **photosynthesis** and **respiration** are energy conversion processes and involve redox reactions.

Photosynthesis is a process that occurs when plants take in carbon dioxide and water to make sugar. Photosynthesis needs solar energy and is catalysed by **chlorophyll**, the green substance in leaves; oxygen is also produced:



For more about photosynthesis, see page 395.

Respiration is a reaction that supplies living organisms with the energy they need. It is the opposite reaction to photosynthesis:



Note that energy is stored in glucose during photosynthesis and released again during respiration.

Respiration involves a series of redox reactions, some of which involve the participation of iron-containing substances called **cytochromes**. Cytochromes are electron carriers. They accept electrons from better reducing agents and give electrons to better oxidizing agents. The iron 'flips' back and forth between Fe^{3+} (the oxidized form) and Fe^{2+} (the reduced form). A similar set of cytochromes are used for the transport of electrons when green plants undergo photosynthesis.

REVISION QUESTIONS

7.1 What are the oxidation numbers of the named element in the following compounds?

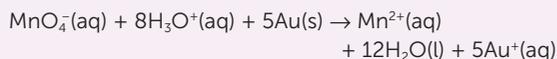
- (i) C in CF_4 (iii) S in SO_4^{2-} (v) N in Mg_3N_2 .
 (ii) Mn in MnO_2 (iv) Sn in SnCl_4

7.2 Use standard electrode potentials to predict whether copper metal could reduce aqueous iron(III) ions to iron(II) at room temperature.

7.3 Using standard electrode potentials, predict if reactions could occur in the following situations. Write balanced redox equations for those reactions that could occur at room temperature.

- (i) An iron nail is placed in an aqueous solution of copper(II) sulfate ($\text{CuSO}_4(\text{aq})$).
 (ii) A silver ring is placed in an aqueous solution of zinc nitrate ($\text{Zn}(\text{NO}_3)_2(\text{aq})$).

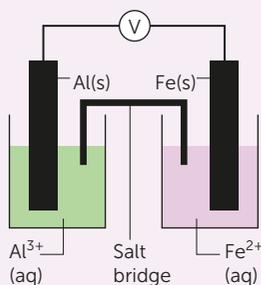
7.4 In the equation



- (i) Which species is oxidized and what is its change in oxidation number?
 (ii) Which species is reduced?
 (iii) Which species is acting as an oxidizing agent?

7.5 When an aqueous solution of iron(III) ions is reacted with sulfur dioxide gas (this forms an acid solution), aqueous iron(II) ions and the sulfate ion (SO_4^{2-}) are produced. Write a balanced overall redox equation for the reaction.

7.6 In the following cell, all solutions are of concentration 1 mol dm^{-3} and at 25°C :



- (i) Mark in the direction of electron flow.
 (ii) Give equations for the processes occurring at each of the electrodes.
 (iii) Calculate E_{cell} .
 (iv) Draw a cell diagram for the system.

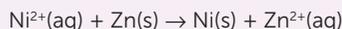
7.7 Tarnished silver jewellery occurs because the silver metal reacts with hydrogen sulfide in the presence of air to form silver sulfide (Ag_2S). The silver object can be 'cleaned' by dipping it into an aqueous solution of sodium chloride, contained in an aluminium metal container.

- (i) Write down symbols for the ions contained in silver sulfide.
 (ii) Using the standard electrode potentials for silver and aluminium, work out if a reaction occurs between the species present in the container.
 (iii) Why is this a more desirable way of cleaning the silver than using silver polish?

7.8 Write a balanced redox equation for the oxidation of concentrated hydrochloric acid (H^+ , Cl^-) to chlorine (Cl_2) by solid manganese(IV) oxide (MnO_2). The manganese(IV) oxide is reduced to $\text{Mn}^{2+}(\text{aq})$.

7.9 In basic solution, zinc metal is oxidized by the nitrate ion ($\text{NO}_3^-(\text{aq})$) to $[\text{Zn}(\text{OH})_4]^{2-}(\text{aq})$. The nitrate ion is reduced to ammonia. Write a balanced ionic equation for this reaction.

7.10 In the reaction



which species is (i) the oxidizing agent, (ii) the reducing agent?

7.11 Chromium plated steel (steel is mostly iron) is often used in motor car bumpers. If the bumper is scratched, will the chromium continue to protect the bumper against rusting?

 Extension material to support this unit is available on our website. The subject of electrolysis is discussed in Appendix 7.

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