

# Chapter

# 4

# ELECTRO-CHEMISTRY AND BATTERIES



**Figure 4.1**

Only a handful of chemicals are responsible for the spectacular effects we see at firework displays. Potassium perchlorate (an oxidant) and aluminium (a reductant) generate large amounts of heat and light. The oxidation of magnesium and aluminium produces brilliant white light. Coloured lights are produced by adding transition metal salts into the firework mixture.

## Introduction

Each New Year's Eve, many Australians celebrate with a fireworks display. These spectacular light shows involve chemical reactions which are examples of oxidation–reduction reactions. Other less spectacular oxidation–reduction reactions include corrosion and the combustion of candle wax. Oxidation–reduction reactions involve the transfer of electrons from one species to another.

In natural biochemical pathways, electron transfer reactions are very important ways of transferring energy. The development of batteries is a practical way of utilising electron transfer reactions as a source of energy.

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# 4.1 OXIDATION AND REDUCTION

## Remember:

Before beginning this section, you should be able to:

- construct word and balanced formulae equations of chemical reactions as they are encountered
- describe the formation of ions in terms of atoms gaining or losing electrons.

## Key content

By the end of this section, you should be able to:

- explain the displacement of metals from solution in terms of transfer of electrons
- identify the relationship between displacement of metal ions in solution by other metals and the relative activity of metals
- account for changes in the oxidation state of species in terms of their loss or gain of electrons.

**half-equation:** an equation that shows gain or loss of electrons

The process of electron loss and electron gain is described using specific terminology. Refer to the **key terms** as you work through this section.

**Figure 4.2**

When a strip of zinc is placed in a blue copper sulfate solution, the zinc becomes coated with metallic copper and the blue colour of the solution fades.

**reductant:** an electron donor; also called a reducing agent

**reduction:** the gain of electrons or decrease in oxidation state

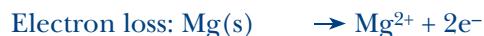
**oxidant:** an electron acceptor; also called an oxidising agent

**oxidation:** the loss of electrons or increase in oxidation state

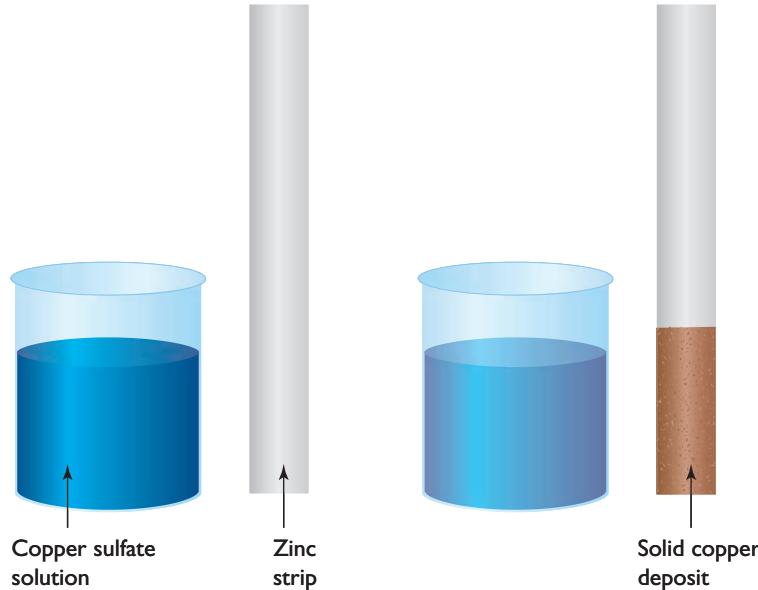
## Electron transfer between metals and cations

The transfer of electrons between atoms, molecules or ions is an important process in many chemical reactions. An important example of electron transfer is the reaction of metals and cations.

In many chemical reactions, metals donate electrons to positive ions (cations). Magnesium, for example, reacts with dilute acids such as hydrochloric acid and sulfuric acid. As the magnesium dissolves, it transfers its valence electrons to the hydrogen ions in the acid solution. The reaction of magnesium metal with hydrogen ions in the acid can be written symbolically as two separate **half-equations**. One half-equation shows the magnesium losing two electrons; the other shows the hydrogen ion gaining the electrons.



Reactive metals can also transfer their valence electrons to other cations. Thus, a piece of zinc placed in a copper sulfate solution quickly becomes coated in metallic copper. In this case the zinc transfers its valence electrons to the copper ions.



## Reductants and oxidants

Metals behave as **reductants**. When metals react with other metal ions, we say they reduce the other metal ions by donating their electrons to these ions. The process of electron gain by the metal ions is called **reduction**.

Metals ions and hydrogen ions behave as **oxidants**. When metal ions react with other metals they remove electrons from the metal. We say that the metal has been **oxidised** by the other metal ion. These types of reactions are commonly referred to as *redox* reactions.

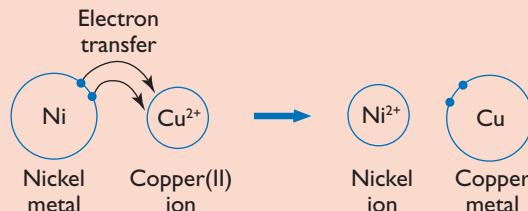
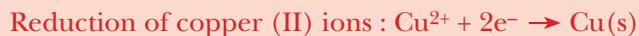
## SAMPLE PROBLEM 4.1

### SOLUTION

The reaction between nickel metal and a solution of copper (II) ions is shown by the following net ionic equation. Discuss the process of oxidation and reduction with reference to this equation.



The equation shows that the solid nickel metal dissolves to produce nickel ions in solution. It also shows that the copper ions in solution are converted to solid copper metal. The nickel metal is the reductant that reduces the copper ions to copper metal. The copper ions are the oxidants that oxidise the nickel metal to nickel ions. This can be shown by the following half-equations:



**Figure 4.3** Nickel metal is a reductant that is oxidised by copper (II) ions.

## SAMPLE PROBLEM 4.2

### SOLUTION



#### METAL DISPLACEMENT

When a strip of magnesium metal is placed in a test tube containing dilute silver nitrate solution, the strip gradually becomes covered with a silvery-grey deposit of crystals. The crystals are separated and analysed and found to be silver metal. The balanced net ionic equation for the reaction is:



Write half-equations for the oxidation of the reductant and the reduction of the oxidant.

The magnesium is the reductant and is oxidised by silver ions to form magnesium ions. The silver ions are the oxidants and they are reduced by the magnesium to form silver metal. The net ionic equation is the sum of the two half-equations written below. (Note that the reduction half-equation is multiplied by 2 so that the electrons cancel when the half-equations are added together).



The loss or gain of electrons is one way of describing redox reactions. Another way is to describe the reaction in terms of changes in oxidation states.

**oxidation state:** a number given to an atom to indicate (theoretically) the number of electrons it has lost or gained (that is, its state of oxidation); also called oxidation number

## Oxidation states

The **oxidation state** of an element is a measure of its degree of oxidation. Elements are assigned oxidation states (written as Roman numerals) according to the assumption that all bonds in compounds are ionic. Although this is not true for many compounds, the concept is useful in explaining redox reactions. Let us examine the oxidation state rules set out in Table 4.1. Some oxidation states are positive and some are negative. Apart from those rules, the oxidation states of oxygen and hydrogen are as follows.



### Oxidation states of hydrogen and oxygen

Oxygen (in most oxide compounds) has an oxidation state of  $-\text{II}$   
Hydrogen (in most hydrogen compounds) has an oxidation state of  $+\text{I}$

**Figure 4.4**

Various solutions of chromium compounds are shown in the photograph. The differences in colour are due to the different oxidation states (OS) of chromium. Clockwise from the green solution:  $\text{CrCl}_3$  (OS =  $+\text{III}$ );  $\text{K}_2\text{CrO}_4$  (OS =  $+\text{VI}$ );  $\text{Cr}(\text{NO}_3)_3$  (OS =  $+\text{III}$ );  $\text{CrCl}_2$  (OS =  $+\text{II}$ );  $\text{K}_2\text{Cr}_2\text{O}_7$  (OS =  $+\text{VI}$ ).

**Table 4.1** Rules for assigning oxidation states to elements

Category	Oxidation state (OS)	Examples
elements (free)	0	copper metal: OS(Cu) = 0 chlorine gas: OS(Cl) = 0
simple ions	charge on the ion	$\text{Cu}^{2+}$ ion: OS( $\text{Cu}^{2+}$ ) = $+\text{II}$ $\text{Cl}^-$ ion: OS( $\text{Cl}^-$ ) = $-\text{I}$
polyatomic ions	sum of the oxidation states of each element must sum to the charge on the ion	sulfate ion ( $\text{SO}_4^{2-}$ ): OS(S) = $+\text{VI}$ OS(O) = $-\text{II}$ $[(+\text{VI}) + 4(-\text{II})] = 2-$
molecular compounds	sum of the oxidation states of each element must sum to zero	sulfur dioxide ( $\text{SO}_2$ ): OS(S) = $+\text{IV}$ OS(O) = $-\text{II}$ $[(+\text{IV}) + 2(-\text{II})] = 0$

Table 4.1 shows us that all uncombined elements have a zero oxidation state. Their ions, however, have positive oxidation states or negative oxidation states depending on whether electrons have been lost or gained to form the ion. Thus copper ions have a higher oxidation state ( $+\text{II}$ ) than chloride ions ( $-\text{I}$ ). In polyatomic ions the oxidation states of each element add together to give the charge on the ion. In the sulfate ion the sulfur has a high oxidation state ( $+\text{VI}$ ) whereas each oxygen has a low oxidation state ( $-\text{II}$ ). The sum of these oxidation states is equal to the charge on the sulfate ion ( $2-$ ). In sulfur dioxide, the sulfur atom is not as highly oxidised as it is in sulfate ions. In sulfur dioxide, the sulfur is in a  $+\text{IV}$  oxidation state.

Oxidation states can be used to describe the oxidation and reduction processes in redox reactions.

**Generally:**

Oxidation = increase in oxidation state

Reduction = decrease in oxidation state

Thus, in a redox reaction, the oxidation state of the reductant increases and the oxidation state of the oxidant decreases.

**SAMPLE PROBLEM 4.3**

**SOLUTION**

Identify the oxidant and reductant in each of the following redox reactions using the method of oxidation states.



- (a) The oxidation states of each element in each reactant and product are shown in the table.

Na	Cl <sub>2</sub>	NaCl
OS(Na) = 0	OS(Cl) = 0	OS(Na <sup>+</sup> ) = +I OS(Cl <sup>-</sup> ) = -I

Thus, Cl<sub>2</sub> is the oxidant as it has been reduced. Its oxidation state has been reduced from 0 to -I.

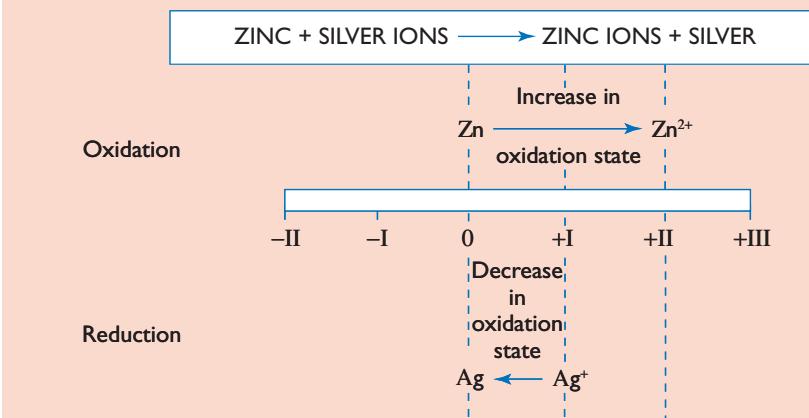
Na is the reductant as it has been oxidised. Its oxidation state has increased from 0 to +I.

- (b) The oxidation states of each element in each reactant and product are shown in the table.

K	H <sub>2</sub> O	KOH	H <sub>2</sub>
OS(K) = 0	OS(H) = +I OS(O) = -II	OS(K <sup>+</sup> ) = +I OS(O) = -II OS(H) = +I	OS(H) = 0

Thus, H<sub>2</sub>O is the oxidant as the H has been reduced. The oxidation state of the H atom has been reduced from +I to 0.

K is the reductant as it has been oxidised. The oxidation state of potassium has increased from 0 to +I.



**Figure 4.5** When a species is oxidised, its oxidation state is increased. Reduction involves a decrease in oxidation state.

## SAMPLE PROBLEM 4.4

### SOLUTION

Demonstrate that the oxidation states of hydrogen and oxygen in the following compounds are not -II and +I respectively.

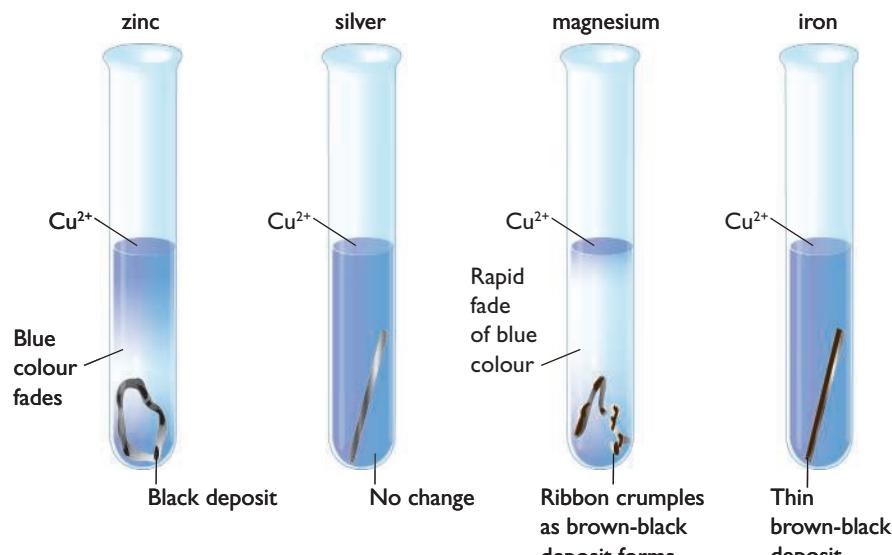
- (a)  $\text{Na}_2\text{O}_2$ , sodium peroxide
- (b)  $\text{BaH}_2$ , barium hydride

(a) Sodium peroxide is an ionic salt composed of sodium ions ( $\text{Na}^+$ ) and peroxide ions ( $\text{O}_2^{2-}$ ). The oxidation state of oxygen is -I (not -II) as the sum of the oxidation states must equal the charge on the ion.

$$(-\text{I}) + (-\text{I}) = 2-$$

(b) Barium hydride is an ionic compound composed of barium ions ( $\text{Ba}^{2+}$ ) and hydride ions ( $\text{H}^-$ ). The oxidation state of hydrogen is -I (not +I), as the oxidation state of the two hydrides must sum to equal the charge on the barium ion.

## Metal displacement reactions and the activity series



**Figure 4.6**

Metal displacement experiments can be used to rank metals in order of their strengths as reductants.

In the previous section we discussed examples of the redox reactions occurring between metals and metal ions. These reactions are commonly called *metal displacement* reactions because as one metal reacts and dissolves the other metal comes out of solution as a solid deposit. These displacement reactions can be used to create an activity series of metals related to their strength as reductants.

Consider the results of the following experiments in which four different metals (zinc, silver, magnesium and iron) are placed in test tubes containing copper (II) sulfate solution (Figure 4.6). The results of this investigation are summarised in Table 4.2.

**Table 4.2** Results of metal displacement experiments

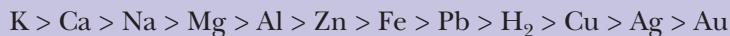
Reducant	Observations
zinc	zinc granule becomes covered in a dark coloured deposit; blue solution slowly fades in colour
silver	no observable reaction
magnesium	very rapid formation of a brown-black coating on the magnesium strip; magnesium crumbles; blue solution rapidly decolourises
iron	iron wire very slowly darkens as a brown-black deposit forms; blue solution very slowly fades in colour

These results allow us to establish an order of activity for these metals. Because the metals act as reductants, this order is also related to their strength as reductants. This order is from most active to least active:



By comparing the reactions of a much wider variety of metal reductants with various metal ion oxidants, the relative ease of oxidation can be ranked for common metals (and hydrogen).

### **Reducants**

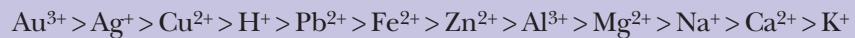


Generally:

- active metals are strong reductants
- inactive metals are weak reductants.

If we experimentally compare the strengths of metal ions as oxidants, then we obtain a result that is in the reverse order. In this case the cations of inactive metals (such as gold) are much stronger oxidants than cations of active metals such as sodium.

### **Oxidants**



Generally:

- cations of inactive metals are strong oxidants
- cations of active metals are weak oxidants.

The generalisations discussed above help us to make predictions about the occurrence of displacement reactions between metals and metal ion solutions. A displacement reaction will occur only if the metal and the metal ion can successfully donate and accept electrons. The following table of half-equations listed in the order of decreasing reductant strength will help us make these predictions. The table shows the strongest reductants at the top right and the strongest oxidants at the bottom left. The half-equations are also written with reversible arrows, indicating that the direction of the reaction can be reversed under different circumstances.

**Table 4.3** Reduction half-equations

Oxidant + electrons $\rightleftharpoons$ reductant
$\text{K}^+ + \text{e}^- \rightleftharpoons \text{K(s)}$
$\text{Ca}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ca(s)}$
$\text{Na}^+ + \text{e}^- \rightleftharpoons \text{Na(s)}$
$\text{Mg}^+ + 2\text{e}^- \rightleftharpoons \text{Mg(s)}$
$\text{Al}^{3+} + 3\text{e}^- \rightleftharpoons \text{Al(s)}$
$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn(s)}$
$\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe(s)}$
$\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb(s)}$
$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$
$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu(s)}$
$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag(s)}$
$\text{Au}^{3+} + 3\text{e}^- \rightleftharpoons \text{Au(s)}$

The following rule can be used in conjunction with the table of reduction half-equations to predict whether or not a reaction will occur between a metal and a metal ion in solution.

**Rule:**

A spontaneous redox reaction will occur if the reductant is higher in the reduction half-equation table than the oxidant.

### SAMPLE PROBLEM 4.5 ➤

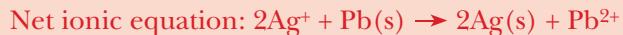
### SOLUTION ➤➤➤➤

Use the information in Table 4.3 to predict whether a spontaneous redox reaction will occur if the following reactants are combined. If a reaction occurs, write the reduction and oxidation half-equations and the net ionic equation for the reaction.

- (a) Lead metal is added to a solution of silver nitrate.
- (b) Copper metal is added to a solution of zinc sulfate.
- (a) Using the rule, we see that lead (the reductant) is higher in the table than silver ions (the oxidant). Thus a spontaneous redox reaction will occur. The table can be used to extract the two half-equations. The oxidation half-equation is obtained by reversing the lead reduction half-equation. Note that single arrows rather than reversible arrows are now used.



Multiply the reduction half-equation by 2 to obtain two electrons that will cancel with the two electrons in the oxidation half-equation to obtain the net ionic equation.



- (b) Using the rule, we see that copper (the reductant) is lower in the table than the zinc ion (the oxidant). Thus, no spontaneous reaction will occur when the substances are mixed.

## SYLLABUS FOCUS

### 10. USING INSTRUCTION TERMS CORRECTLY

When answering questions it is important to know what the instruction terms ('verbs') require you to do. Here is an example:

**'Distinguish'**

This instruction word requires you to recognise differences between objects, processes or concepts.

**Example:**

Distinguish, using an appropriate example, between the processes of oxidation and reduction in terms of the concept of oxidation states.

**Answer:**

Oxidation is the process in which an element increases its oxidation state and reduction is the process in which an element decreases its oxidation state. Thus, when iron reacts with chlorine to form iron (III) chloride, the iron is oxidised as its oxidation state increases from 0 to +III. The chlorine is reduced as its oxidation state decreases from 0 to -I.

## 4.1 Questions

1. Felicity decided to investigate metal displacement reactions. She was provided with samples of cobalt metal as well as three electrolyte solutions. Felicity placed samples of the cobalt metal in three different electrolytes and she made the following observations:

Electrolyte	Observations
dilute sulfuric acid	<ul style="list-style-type: none"> <li>slow bubbling of a colourless gas</li> <li>solution goes pink as cobalt slowly dissolves</li> </ul>
silver nitrate solution	<ul style="list-style-type: none"> <li>rapid formation of a flaky silver coating on the surface of the cobalt</li> <li>significant rise in temperature</li> <li>solution gradually turns pink</li> </ul>
zinc sulfate solution	<ul style="list-style-type: none"> <li>no visible changes</li> </ul>

Use the above experimental data to answer each question.

- (a) Rank the following oxidants in decreasing order of strength.



- (b) Rank the following reductants in decreasing order of strength.



- (c) Determine whether the following statements are true or false.

- (i) Cobalt is a stronger reductant than zinc.  
(ii) Cobalt is a weaker reductant than silver.

2. Answer true or false to each of the following statements.

- (a) Metallic lead displaces gold from a gold (III) nitrate solution.  
(b) If a silver strip is placed in a magnesium sulfate solution, crystals of magnesium form on the silver strip.  
(c) Calcium reacts readily with dilute hydrochloric acid.

3. Determine whether a spontaneous redox reaction will occur when the following substances are mixed. Where a reaction occurs, write the reduction and oxidation half-equations and the net ionic equation.

- (a) magnesium metal + silver nitrate solution  
(b) iron metal + lead (II) nitrate solution  
(c) silver metal + aluminium sulfate solution

4. Jason adds mercury to a solution of gold (III) nitrate. He observes that gold metal is displaced from solution. Jason then tests a lead (II) nitrate solution with mercury and finds that no reaction occurred.

- (a) Use Jason's experimental data to rank the metals mercury, lead and gold in order of decreasing reductant strength. Justify your answer.  
(b) Describe an experiment that Jason can perform to determine whether mercury is a stronger or weaker reductant than silver.

5. Sarah tested three metals — tin, nickel and cobalt — to determine their strengths as reductants. She used metal displacement reactions to classify the metals. The table below shows the results of her investigation. A tick (✓) indicates that a displacement reaction occurs, and a cross (✗) indicates that there was no observable reaction.

	Tin	Nickel	Cobalt
tin (II) ions	✗	✓	✓
nickel (II) ions	✗	✗	✓
cobalt (II) ions	✗	✗	✗

- (a) Rank the metals from strongest reductant to weakest reductant.  
(b) Rank the metal ions from strongest oxidant to weakest oxidant  
(c) Write the net ionic equations for each displacement reaction observed.

6. Rani placed 500 mL of 0.20 mol/L copper (II) sulfate solution into a large beaker, and stirred excess zinc powder into the solution. The mixture was left until the reaction was complete.

- (a) Write a net ionic equation for the redox reaction.  
(b) Use the method of oxidation states to determine the reductant and the oxidant.  
(c) Calculate the mass of copper that would have been displaced from the solution.

7. Determine the oxidation state of the indicated element in each of the following.
- Mn in  $\text{MnO}_4^-$
  - Cr in  $\text{Cr}_2\text{O}_7^{2-}$
  - Cl in  $\text{Cl}_2\text{O}_7$
  - V in  $\text{V}_2\text{O}_5$
  - I in  $\text{KIO}_3$
8. Historically, the process of oxidation referred to reactions in which a substance gained oxygen. Thus, magnesium was oxidised when it burnt in oxygen to form magnesium oxide. Distinguish between this historical definition of oxidation and other definitions, and discuss these differences using the magnesium oxide example.

## 4.2 GALVANIC CELLS AND BATTERIES

### Remember:

Before beginning this section, you should be able to:

- construct word and balanced formulae equations of chemical reactions as they are encountered
- describe the formation of ions in terms of atoms gaining or losing electrons.

### Key content

By the end of this section, you should be able to:

- describe and explain galvanic cells in terms of oxidation/reduction reactions.
- outline the construction of galvanic cells and trace the direction of electron flow
- define the terms *anode*, *cathode*, *electrode* and *electrolyte* to describe galvanic cells
- perform a first-hand investigation to identify the conditions under which a galvanic cell is produced
- perform a first-hand investigation and gather first-hand information to measure the difference in potential of different combinations of metals in an electrolyte solution
- gather and present information on the structure and chemistry of a dry cell or lead-acid cell, and evaluate it:
  - in comparison to one of the following: button cell, fuel cell, vanadium redox cell, lithium cell, liquid junction photovoltaic device (e.g. the Gratzel cell)
  - in terms of chemistry, cost and practicality, impact on society, and environmental impact
- solve problems and analyse information to calculate the potential  $E^\ominus$  requirement of named electrochemical processes using tables of standard potentials and half-equations.

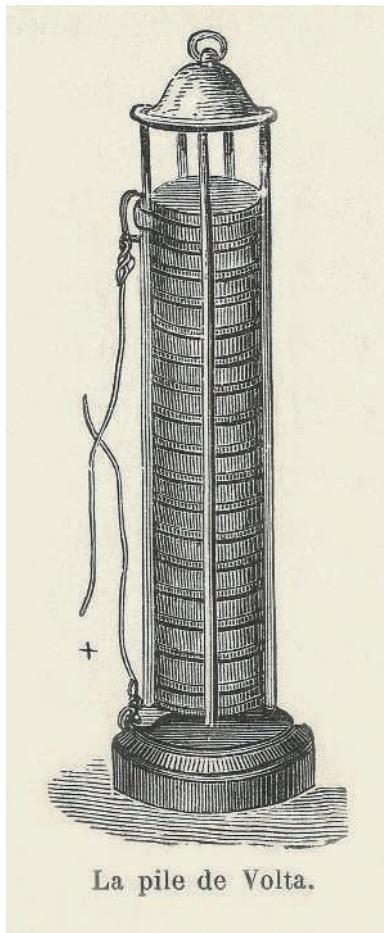
### Galvanic cells

The pioneering work in the development of electrochemical cells and batteries began in Italy. In 1791, the Italian scientist Luigi Galvani investigated the connection between metals and electricity using frog muscles. He observed that if two different metals were inserted into frog leg muscle, an electric current was generated.

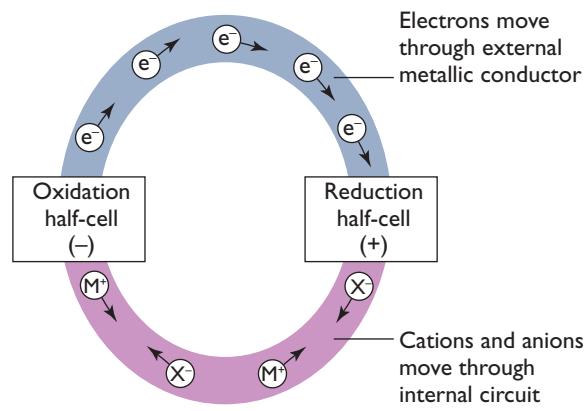
During the period 1794 to 1800, the Italian scientist, Alessandro Volta, discovered that frog's leg muscles were not needed to generate the electricity. He found that a bowl of salt water could be substituted for the frog muscle and an electric current generated. He also found that using several bowls of salt water and alternating copper and zinc electrodes in

series generated a higher voltage. This was the first working battery. Volta later refined this battery by using metallic zinc and copper coins arranged in a vertical pile and separated by cardboard soaked in salt water. These 'voltaic piles' could be made to generate considerable currents by increasing the number of coins in the pile.

These early devices are examples of electrochemical cells. We now call them **galvanic cells** in honour of Luigi Galvani. Galvanic cells are readily constructed from combinations of metals (electrodes) and electrolytes. The basic structure of all galvanic cells is shown in Figure 4.8. The cell is constructed from two **half-cells**. One half-cell is the *oxidation half-cell*; the other is the *reduction half-cell*.



**Figure 4.7** Volta's pile was the first battery. It consisted of alternating layers of zinc and copper disks or coins separated by pieces of paper, or felt, soaked in salt solution. The zinc disk at one end formed the negative electrode and the copper disk at the other end, the positive electrode.



**Figure 4.8**

Galvanic cells consist of two half-cells linked by a metallic conductor (externally) and a salt bridge (internally).

**galvanic cell:** an arrangement of electrodes and electrolytes in which a redox reaction causes a flow of electricity; also called an electrochemical cell

**half-cell:** either the oxidation or reduction half of an electrochemical cell

**electrode:** the metallic conducting plates of a galvanic cell

**anode:** the electrode at which oxidation takes place. This electrode is negative in a galvanic cell.

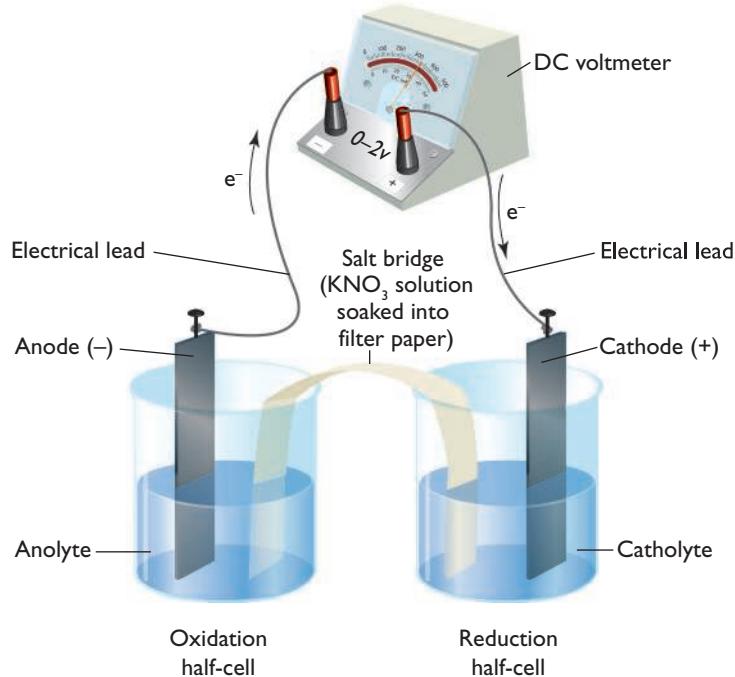
**cathode:** the electrode at which reduction takes place. This electrode is positive in a galvanic cell.

**electrolyte:** a substance that releases ions when in solution or when melted and that carries an electric current

**salt bridge:** an electrolyte or electrolyte gel that joins two half-cells in a galvanic cell and allows movement of ions to maintain a balance of charges; also called an ion bridge

### Setting up a simple galvanic cell

In a galvanic cell there are two conducting terminals called **electrodes**. One electrode is called the **anode** and the other the **cathode**. When the cell is operating, electrons leave the negative anode of the oxidation half-cell and travel to the positive cathode of the reduction half-cell through a conducting wire in response to a potential difference between the half-cells. A voltmeter is not required in the circuit. It is connected to the two electrodes only when we want to measure the difference in electric potential or voltage between the half-cells. Electrons and charges will not flow unless a complete circuit is present. An **electrolyte** or electrolyte gel is required for ions to move through the internal circuit as electrons move through the external circuit. In the electrolyte, cations move towards the reduction half-cell and anions move towards the oxidation half-cell. Solutions of nitrate salts such as potassium nitrate are commonly used as a **salt bridge** (or ion bridge) in simple galvanic cells. Alternatively, a porous partition is used, through which ions can slowly diffuse.



**Figure 4.9**

In the school laboratory a simple galvanic cell can be set up using beakers, wires and filter papers soaked in electrolyte solution.

In the school laboratory it is quite simple to construct and investigate galvanic cells. Figure 4.9 shows two beakers containing the electrodes and electrolytes. These represent the two half-cells. Filter paper soaked in saturated potassium nitrate solution is often used as the salt bridge that links the two beakers. The external circuit is completed using an electrical lead to link the two electrodes.

### Galvanic cell notation

A simpler way of expressing this galvanic cell structure is to use a cell diagram. Consider a cell in which one half-cell is composed of a zinc electrode in a zinc nitrate solution and the other is made from a copper electrode in a copper (II) nitrate solution. The cell notation for this galvanic cell is:



**redox couple:** the oxidant–reductant pair in a half-equation

**anolyte:** the electrolyte present in the anode compartment

**catholyte:** the electrolyte present in the cathode compartment



### GALVANIC CELL

#### SAMPLE PROBLEM 4.6

Anojian conducted a series of experiments on galvanic cells in which an Fe | FeSO<sub>4</sub> couple was used as a reference half-cell. For the other half-cell, he used one of the following test couples:

- (i) Zn | ZnSO<sub>4</sub>, (ii) Mg | MgSO<sub>4</sub>, (iii) Cu | CuSO<sub>4</sub>.

In each case:

- a 1.0 mol/L electrolyte solution was used
  - a DC voltmeter was used to measure the potential difference for each galvanic cell
  - the couples were connected to obtain a positive voltage.
- The results of Anojian's experiments are tabulated below.

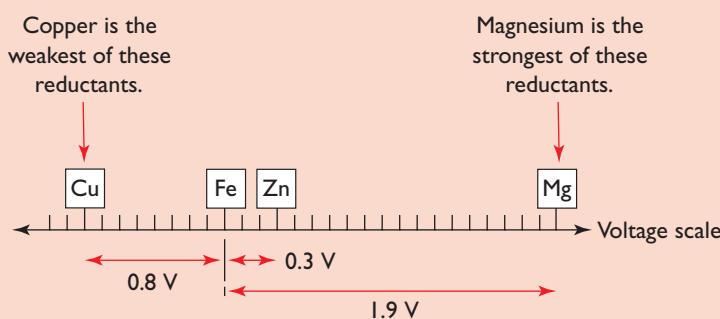
Run	Couple 1	Couple 2	Couple connected to negative voltmeter terminal	Voltmeter reading (V)
1	Zn   ZnSO <sub>4</sub>	Fe   FeSO <sub>4</sub>	Zn   ZnSO <sub>4</sub>	+ 0.3
2	Mg   MgSO <sub>4</sub>	Fe   FeSO <sub>4</sub>	Mg   MgSO <sub>4</sub>	+ 1.9
3	Fe   FeSO <sub>4</sub>	Cu   CuSO <sub>4</sub>	Fe   FeSO <sub>4</sub>	+ 0.8

Discuss Anojian's results in relation to the activity series of metals and the loss or gain of electrons by each half-cell.

## SOLUTION

These results are consistent with the activity series in which magnesium is a stronger reductant than zinc, zinc is a stronger reductant than iron and iron is a stronger reductant than copper. The greatest voltage is obtained when the couple containing the most active metal (magnesium) is connected to the couple containing the least active metal (copper). The relative ease of oxidation of each metal can be determined from these results. Magnesium is more readily oxidised than zinc; copper is less readily oxidised than iron. (Note the last line in the table where the iron couple has swapped position to obtain a positive voltage.)

Figure 4.10 shows how these voltage readings are related to a voltage scale.

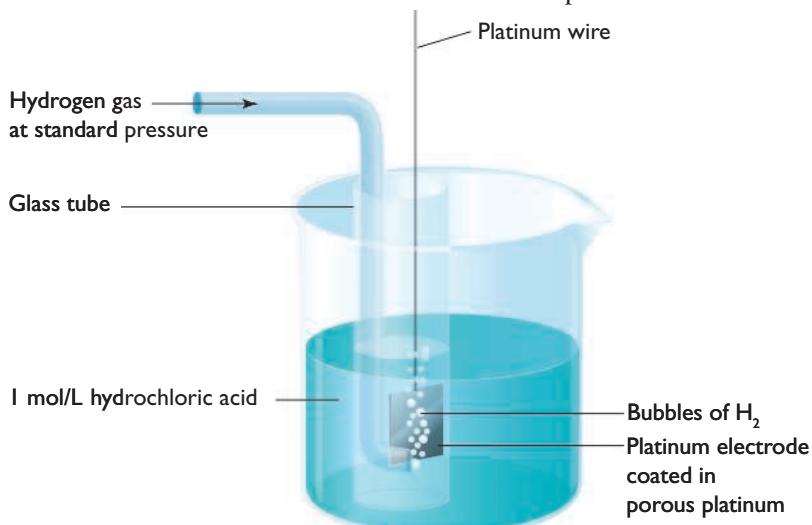


**Figure 4.10** The voltage readings in this experiment are the differences between the electrode potentials of each half-cell.

## Standard electrode potentials

To obtain reliable and reproducible results when constructing galvanic cells it is important to specify a set of standard conditions. These are:

- electrolyte concentration = 1.0 mol/L
- standard temperature = 25°C
- standard pressure = 100 kPa.



**Figure 4.11**

The standard hydrogen half-cell is assigned an electrode potential of 0.00V.

In addition, a standard reference half-cell is used to compare other test half-cells. This standard is the standard hydrogen half-cell ( $\text{Pt}, \text{H}_2|\text{H}^+$ ). This half-cell consists of an inert platinum electrode covered in ‘platinum black’, which is a highly porous form of platinum metal powder. This electrode is placed in a 1.0 mol/L solution of hydrogen ions and pure hydrogen gas is bubbled over the surface of the electrode under conditions of standard temperature and pressure (Figure 4.11).

The reduction half-equation for this half-cell is:



The standard hydrogen half-cell is assigned a half-cell potential of zero volts. Thus, when a test half-cell (e.g. M | M<sup>+</sup>) is connected to the standard hydrogen half-cell (Pt, H<sub>2</sub> | H<sup>+</sup>) in a galvanic cell, the measured voltage (or standard cell potential) is equal to the half-cell potential of the test couple.



**cell potential:** the difference between the electrode potentials of the half-cells of a galvanic cell; also called voltage

**reduction potential:** the potential of a reduction half-cell relative to the standard hydrogen electrode; also called electrode potential

### Rules for predicting a spontaneous redox reaction

1. Reduction: Examine the table and select the correct reduction half-equation. Record the reduction potential for this half-equation.
2. Oxidation: Examine the table and select the oxidation half-equation by reversing the appropriate reduction half-equation. Record the oxidation potential by changing the sign of the half-cell potential.
3. Electron balance: Balance the electrons in the two half-equations by multiplying by an appropriate factor.
4. Cell equation: Add the reduction half-equation to the oxidation half-equation.
5. Cell potential: Add the reduction potential to the oxidation potential to obtain the cell potential.
6. Spontaneity: A positive cell potential is indicative of a spontaneous redox reaction in the forward direction.

The standard **cell potential** ( $E^\ominus$ ) is defined as the sum of the standard half-cell reduction potential and the standard half-cell oxidation potential.

$$\begin{aligned} E^\ominus &= E^\ominus_{\text{reduction}} + E^\ominus_{\text{oxidation}} \\ E^\ominus &= E^\ominus(\text{M}^+ \mid \text{M}) + (\text{H}^+ \mid \text{H}_2, \text{Pt}) \\ E^\ominus &= E^\ominus(\text{M}^+ \mid \text{M}) + 0.00 \\ E^\ominus &= E^\ominus(\text{M}^+ \mid \text{M}) \end{aligned}$$

The value of the standard cell potential may be positive or negative, depending on whether the test cell acts as a site of oxidation or a site of reduction.

Tables of standard cell potentials are published in reference books. They are referred to as standard **reduction potentials** as the ( $E^\ominus$ ) values refer to reduction half-equations. Table 4.4 represents a shortened version of the reduction potential table. An extended version of this table appears in the Appendix.

**Table 4.4** Table of standard reduction potentials

Equation	$E^\ominus$ (volts)
$\text{K}^+ + \text{e}^- \rightleftharpoons \text{K(s)}$	-2.94
$\text{Ba}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ba(s)}$	-2.91
$\text{Ca}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ca(s)}$	-2.87
$\text{Na}^+ + \text{e}^- \rightleftharpoons \text{Na(s)}$	-2.71
$\text{Mg}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mg(s)}$	-2.36
$\text{Al}^{3+} + 3\text{e}^- \rightleftharpoons \text{Al(s)}$	-1.68
$\text{Mn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mn(s)}$	-1.18
$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn(s)}$	-0.76
$\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe(s)}$	-0.44
$\text{Ni}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ni(s)}$	-0.24
$\text{Sn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Sn(s)}$	-0.14
$\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb(s)}$	-0.13
$\text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2\text{(g)}$	0.00
$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu(s)}$	+0.34
$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag(s)}$	+0.80

The reduction potential table (table 4.4) is arranged with the strongest oxidants in the lower left-hand corner and the strongest reductants in the upper right-hand corner of the left-hand column.

This table can be used to predict whether a redox reaction is spontaneous in the forward direction. These predictions rely on standard conditions being met. If concentrations change, for example, then the predictions may not be accurate.

## SAMPLE PROBLEM 4.7

## SOLUTION

- (a) Use the table of standard reduction potentials to determine the standard cell potential for the following galvanic cell.



- (b) Write the oxidation half-equation, the reduction half-equation and the net ionic equation for this galvanic cell.

- (c) A student used a standard  $\text{Cu(s)} \mid \text{Cu}^{2+}$  couple as one half-cell. The other half-cell was composed of a metal, M, in a 1.0 molar solution of  $\text{M}^{2+}$  ions. The galvanic cell was found to have a potential difference of +2.70 V when the copper couple was connected to the positive voltmeter terminal. Identify the  $\text{M} \mid \text{M}^{2+}$  couple.

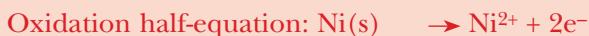
- (a) The cell potential is the sum of the reduction potential for the reduction half-cell and the oxidation potential for the oxidation half-cell.

$$\begin{aligned} E^\ominus &= E^\ominus_{\text{reduction}} + E^\ominus_{\text{oxidation}} \\ &= E^\ominus (\text{Ag}^+ \mid \text{Ag}) + E^\ominus (\text{Ni} \mid \text{Ni}^{2+}) \\ &= (+0.80) + (+0.24) \\ &= +1.04 \text{ V} \end{aligned}$$

Note: The -0.24 V reduction potential for nickel has become +0.24 V for oxidation.

The positive cell potential indicates that the reaction is spontaneous in the forward direction. Nickel will act as the anode and silver will act as the cathode.

- (b) The oxidation half-equation is the reverse of the one published in the data table.



(Multiply by 2 before adding.)



- (c) Copper is the cathode as it is the positive electrode. M is the anode and therefore is a more active metal than copper.

$$\begin{aligned} E^\ominus &= E^\ominus_{\text{reduction}} + E^\ominus_{\text{oxidation}} \\ +2.70 &= E^\ominus (\text{Cu}^{2+} \mid \text{Cu}) + E^\ominus (\text{M} \mid \text{M}^{2+}) \\ +2.70 &= (+0.34) + E^\ominus (\text{M} \mid \text{M}^{2+}) \end{aligned}$$

$$\begin{aligned} \text{Thus, } E^\ominus (\text{M} \mid \text{M}^{2+}) &= (+2.70) - (+0.34) \\ &= +2.36 \text{ V} \end{aligned}$$

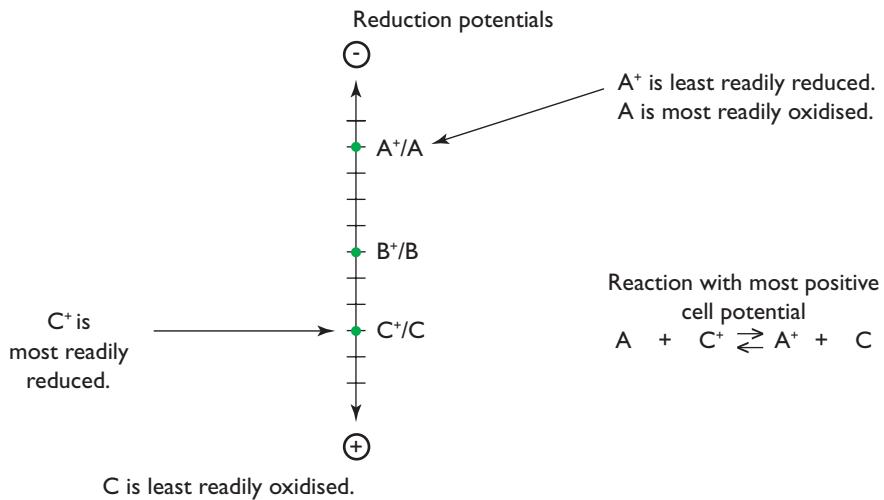
This is the oxidation potential for metal M, so the reduction potential is -2.36 V. On examining the table of electrode potentials this reduction potential corresponds with the magnesium-magnesium-ion couple.

### Review

**Reduction:** The more positive the reduction potential the greater the tendency for reduction to occur.

**Oxidation:** The more positive the oxidation potential the greater the tendency for oxidation to occur.

**Spontaneity:** Spontaneous redox reactions occur in the direction in which the cell potential is positive.



**Figure 4.12**

The cell potential is positive for a spontaneous redox reaction.  
The greater the positive potential the more the equilibrium lies to the right.

## 4.1 PRACTICAL ACTIVITIES

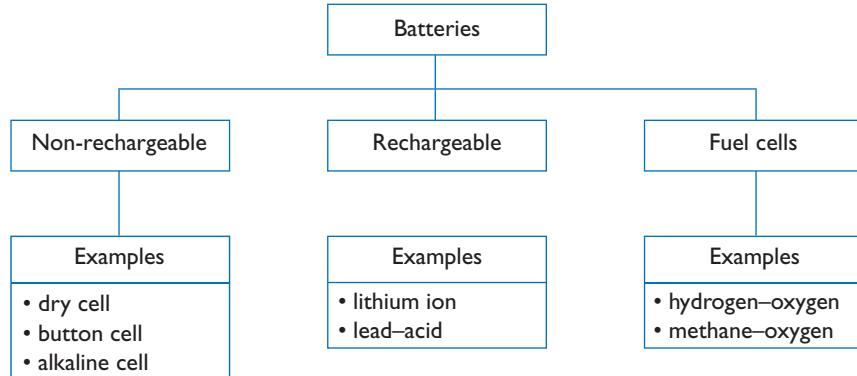
### Galvanic cells

One of the first batteries developed for the space program in the 1960s was the silver–zinc battery. These have a relatively short life cycle. The 1997 Mars Pathfinder mission used a rechargeable silver–zinc battery.

## Batteries

Batteries are very important in our modern world. They are used to power mobile phones and laptop computers as well as many other devices. Batteries are portable sources of electrical energy. Not all electric cells are batteries. The dry cells or alkaline cells that you use in appliances such as a torch consist of only one galvanic cell. Technically, they are ‘cells’ rather than batteries. (The word ‘battery’ normally implies a series of things.) In a car, the lead–acid battery consists of a number of cells connected in series. Because it is composed of more than one cell it is classified as a true battery. When batteries are connected in series, a higher voltage is also obtained.

Batteries and cells can be classified in a variety of ways as shown in Figure 4.13. Dry cells and alkaline cells are common non-rechargeable cells. Nicad batteries, many lithium batteries and lead–acid car batteries are rechargeable. Fuel cells need to be recharged with fuel and an oxidising agent in order to continue producing electrical energy.

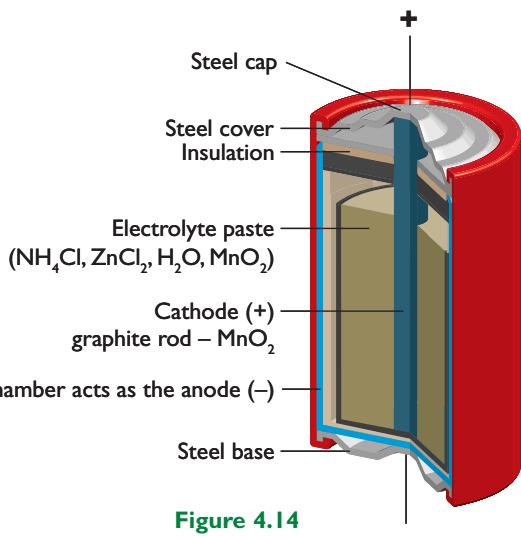


**Figure 4.13**

Batteries can be classified as primary (non-rechargeable) or secondary (rechargeable). Fuel cells require an input of fuel and an oxidant.

## The dry cell

The dry cell (or Leclanché cell) was first developed in 1866 by Georges Leclanché and has remained one of the most common and reliable sources of portable electric power. Part of their appeal lies in their relative cheapness.



**Figure 4.14**

The dry (Leclanché) cell is commonly used in torches, portable radios and CD players.

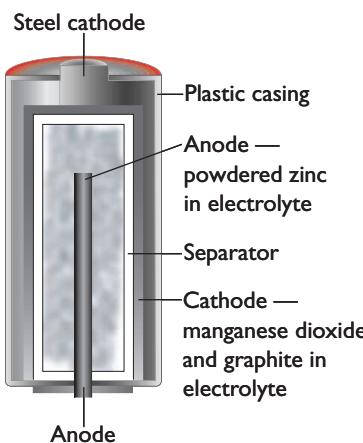
Figure 4.14 shows the typical structure of a dry cell. The central positive cathode consists of an inert graphite rod surrounded by graphite and manganese dioxide powder. The negative anode consists of the zinc casing of the cell. Between the two electrodes is an aqueous electrolyte paste containing ammonium chloride together with more powdered graphite and manganese dioxide.

The chemistry of the dry cell and issues related to its cost and practicality, as well as its effect on society and the environment, are summarised in Table 4.5.

An improved version of the normal dry cell is the more expensive alkaline cell. This 1.5 V cell is used in higher drain appliances. The zinc anode is powdered so that it can deliver a higher, faster current for a longer time. Instead of the acidic paste, the electrolyte consists of a 7-molar potassium hydroxide solution. The cell has a life that is five times as long as a dry cell due to the larger amount of  $\text{MnO}_2$  that is present in the cell.

**Table 4.5** Chemistry of the dry cell

Dry cell feature	Comment
voltage	1.5 V
anode (-)	Zn casing
anode half-equation	$\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+} + 2\text{e}^-$
cathode (+)	$\text{MnO}_2, \text{C}$
cathode half-equation	$2\text{MnO}_2(\text{s}) + 2\text{NH}_4^+ + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2\text{NH}_3$
electrolyte	Aqueous paste of ammonium chloride 26% (w/w)
other information about the battery	The $\text{MnO}_2$ ensures that hydrogen atoms released from the ammonium ions during reduction are converted to water. As the cell operates, $\text{ZnCl}_2$ forms at the anode; this contributes to the conductivity of the paste. The ammonia that forms at the cathode complexes with the zinc ions to form a stable complex ion.
cost and practicality	The materials of the cell are inexpensive and cheap to replace even though the cell is non-rechargeable. These cells have a low energy density. The voltage falls during use, due to a drop in electrolyte concentration around the cathode and the time required for the $\text{Mn}_2\text{O}_3$ to diffuse away from the cathode. These cells have a short shelf life as the zinc is attacked by the ammonium chloride. As well, the zinc casing oxidises during cell discharge and the acidic paste can leak out through cracks and corrode other components.
effect on society	They are used in low-drain appliances such as torches, remote controls, LCD calculators and battery-powered toys that do not require high currents.
effect on the environment	Battery components are weakly acidic and non-toxic. There are few environmental consequences on disposal.



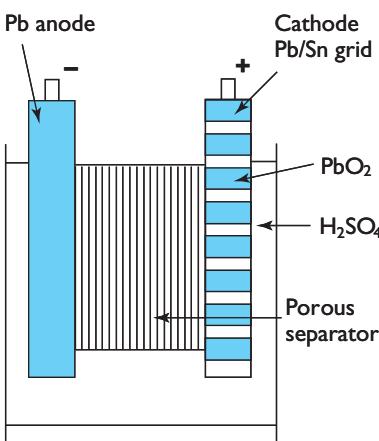
**Figure 4.15**

Alkaline zinc–manganese dioxide cells were developed as a consequence of the greater demand for a higher capacity portable energy source than the dry cell could provide. Alkaline cells have a greater current output.

The first lead–acid battery was invented by the French physician Gaston Planté in 1859. This battery became the first rechargeable battery for commercial use.

**Figure 4.16**

Lead–acid batteries are used in motor vehicles. Each cell consists of two lead electrodes or grids. The grid structure provides a larger surface area for electrode reactions.

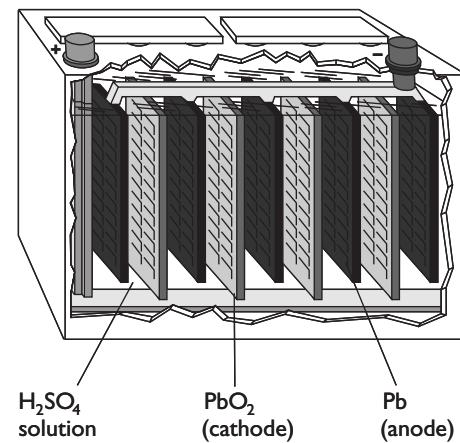


## The lead–acid storage battery

Unlike the dry cell, lead–acid car storage batteries can be recharged by application of an external current. The battery is used during start-up to provide the energy for the car’s starter motor. The battery is gradually recharged during driving using electrical energy from the car’s alternator.

Figure 4.16 shows the structure of a lead–acid storage battery. Six cells, each supplying about 2 V, are arranged in series to produce a battery with a voltage of about 12 V. In each cell the anode is composed of a porous lead sheet, and the

cathode is made of a lead sheet coated in compressed lead (IV) oxide. Each electrode is in the form of a grid to increase the surface area. The electrolyte in each cell is sulfuric acid. In the battery, thin, perforated fibreglass sheets separate each electrode.



The chemistry of the lead–acid storage battery and issues related to its cost and practicality as well as its effect on society and the environment are summarised in Table 4.6.

**Table 4.6** Chemistry of the lead–acid storage battery

Battery features	Comments
voltage	about 12 volts
anode (–)	Pb sheet
anode half-equation	$\text{Pb}(\text{s}) + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^-$
cathode (+)	$\text{PbO}_2$ powder on lead sheet
cathode half-equation	$\text{PbO}_2(\text{s}) + \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$
electrolyte	sulfuric acid (35% w/w)
other information about the battery	<p>The life of the battery is limited by various factors including:</p> <ul style="list-style-type: none"> <li>(a) the lead sulfate disintegrating from the electrode surface affects the ability of the battery to be recharged as it ages</li> <li>(b) slow corrosion of the lead anode</li> <li>(c) internal short circuiting.</li> </ul> <p>During discharge, the density of the electrolyte drops from <math>1.26 \text{ g/cm}^3</math> to <math>1.1 \text{ g/cm}^3</math> as hydrogen ions are consumed. A battery hydrometer can be used to measure the density of the electrolyte and this is used as a measure of the state of charge of the battery.</p>

**Table 4.6** Chemistry of the lead–acid storage battery (*continued*)

Battery features	Comments
cost and practicality	The batteries are expensive due to the lead content. The battery lasts many years and can be recharged over and over again. Batteries can also be recharged externally to the car using a suitable transformer. Care must be taken to avoid too-rapid recharging as explosive hydrogen gas can form. These batteries are heavy and this limits their portability. They have the lowest energy density of most commonly used rechargeable batteries.
effect on society	This is an important battery for car start-up motors as it provides high currents over short periods. Also, it is a useful storage battery for remote locations. It can be recharged by connecting to solar panels or electric generators. Useful for emergency lighting.
effect on the environment	Lead–acid batteries are recycled to retrieve the lead. Lead is toxic to organisms in the environment. It causes anaemia in humans. The electrolyte is highly acidic and can cause severe damage if spilled. Sealed lead–acid cells prevent acid fumes from causing corrosion.



**Figure 4.17**

By measuring the density of the electrolyte in the lead–acid battery the state of charge of the battery can be measured. As the battery discharges, the density of the sulfuric acid electrolyte decreases, allowing the floats in the hydrometer to sink. If the floats are too low, the battery needs recharging.

## 4.2 DATA ANALYSIS

Comparing batteries

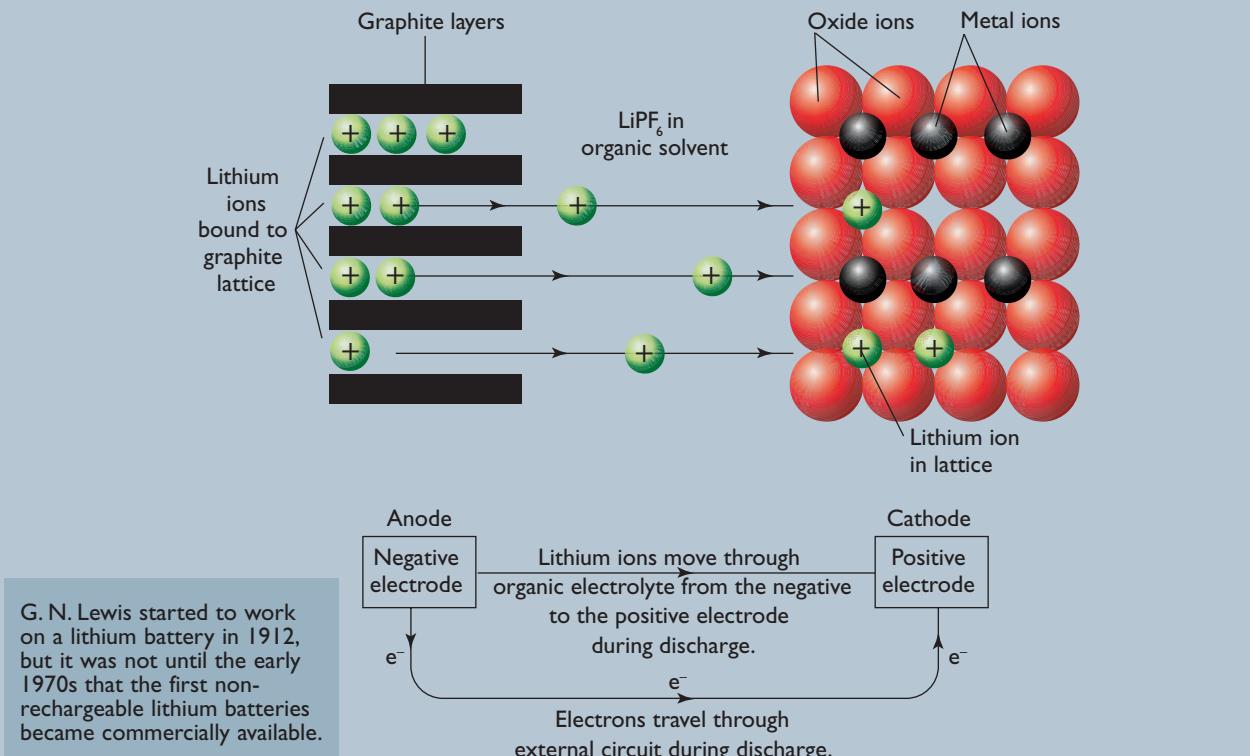
## SYLLABUS FOCUS

### 11. NEW BATTERY TECHNOLOGIES

This box provides information on three new battery technologies: lithium ion batteries, vanadium batteries and liquid-junction photovoltaic (Gratzel) cells. You can select one of these new batteries to study, or you can investigate other common battery types in the Data Analysis Activity 4.2 at the end of this chapter.

#### Lithium ion batteries

Lithium is an active metal, so batteries that use lithium must contain no water, but use non-aqueous solvents instead. Batteries that utilise lithium ions rather than lithium metal are much safer, and it is this type of battery technology that powers mobile phones and laptops. This type of battery has been used in the probes sent to Mars by NASA.



**Figure 4.18** During the operation of a lithium ion battery, lithium ions move from the anode to the cathode.

**Table 4.7** Chemistry of a lithium ion battery

Battery feature	Comment
voltage	3.6 volts
anode (-)	C (graphite) containing $\text{Li}^+$ ions bound to the crystal layers
anode half equation	$\text{Li}_x\text{C}_6 \rightarrow \text{C}_6 + x\text{Li}^+ + xe^-$ ( $x < 1$ )
cathode (+)	lithiated metal oxides (e.g. $\text{LiCoO}_2$ ); contains $\text{Li}^+$ ions bound to the lattice
cathode half equation	$\text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^- \rightarrow \text{LiCoO}_2$ ( $x < 1$ )
electrolyte	$\text{LiPF}_6$ or $\text{LiBF}_4$ in an organic solvent
other information about the battery	Microporous polyethylene membranes separate ions and electrons. During discharge the lithium ions travel from the anode to the cathode. During recharge the lithium ions travel from the cathode back to the anode.

## SYLLABUS FOCUS

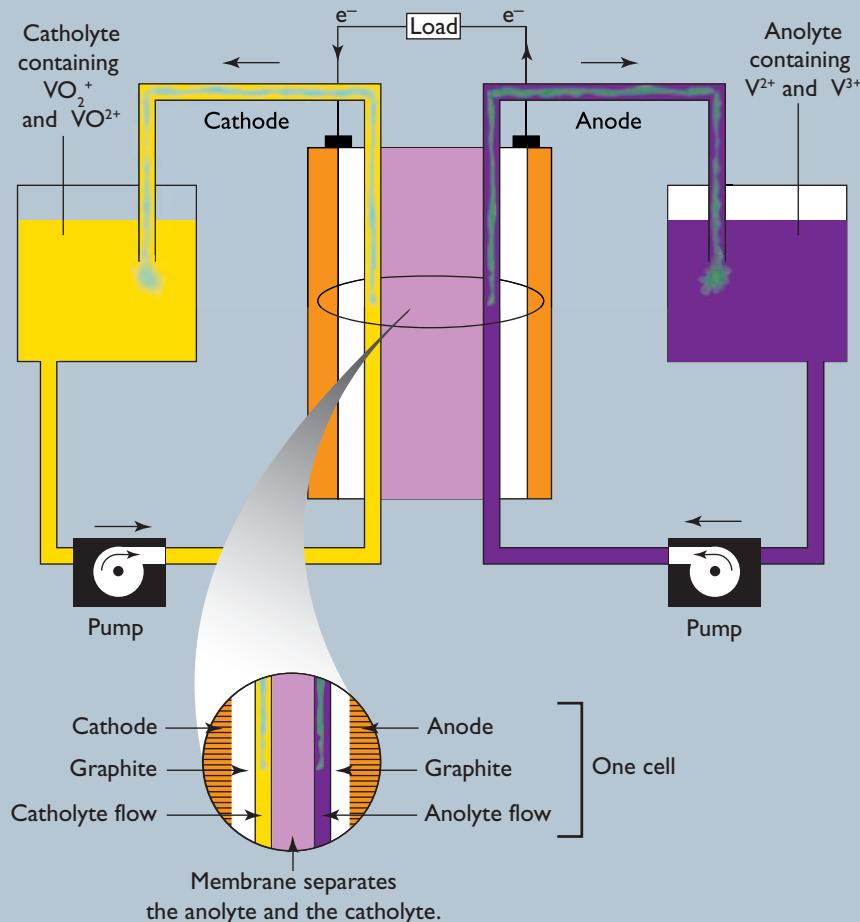
**Table 4.7** Chemistry of a lithium ion battery (continued)

Battery feature	Comment
cost and practicality	More expensive than NICAD batteries. Operates over a wide temperature range. Rechargeable. High energy density (about twice that of a NICAD battery). Low maintenance. No memory effect. Fragile and so needs a protective circuit to limit peak voltages. Low self-discharge. Smaller and lighter than NICADs. Long recharging times.
effect on society	Major uses include laptop and mobile phone batteries as well as satellite batteries. This has had a significant impact on communications technology.
effect on the environment	The components are environmentally safe as there is no free lithium metal.

### Vanadium redox battery

The vanadium battery is a redox flow battery system that was invented by Professor Maria Skyllas-Kazacos and her research team at the University of NSW (UNSW) in 1985. Since that time, the battery has undergone further development leading towards commercialisation.

The vanadium redox battery uses tanks to store two vanadium electrolytes which are pumped through a battery stack where the chemical energy stored in the solutions is converted to electrical energy. The anolyte contains vanadium ions in the +II and +III oxidation states. The catholyte contains vanadium ions in the +IV and +V oxidation states. The potential difference between these two half-cells leads to electron flow in the external circuit.



**Figure 4.19** The vanadium battery is a redox flow battery. Two vanadium electrolytes are pumped through the battery stack and electrical energy is extracted.

## SYLLABUS FOCUS

**Table 4.8**

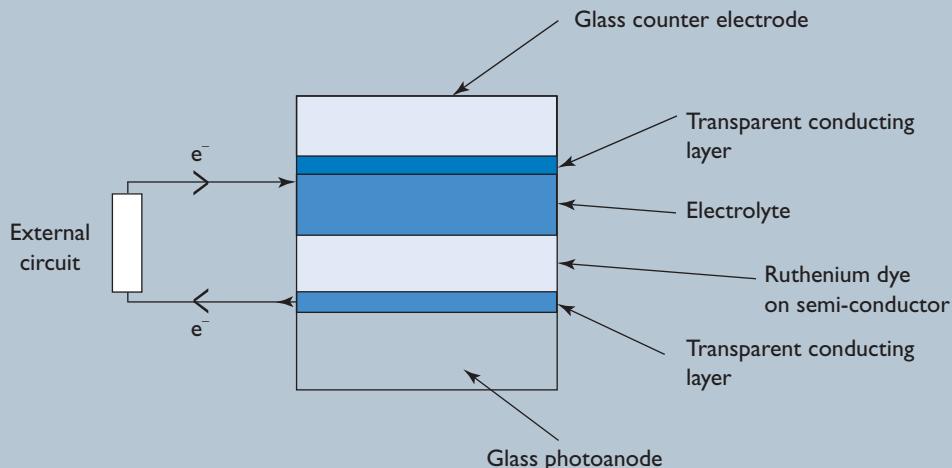
Battery feature	Comment
voltage	1.26 volts
anode (-)	bipolar electrodes composed of graphite impregnated polypropylene sheet or graphite felt
anode half-equation	$V^{2+} \rightarrow V^{3+} + e^-$
cathode (+)	bipolar electrodes composed of graphite impregnated polypropylene sheet or graphite felt
cathode half-equation	$VO_2^+ + 2H^+ + 2e^- \rightarrow VO^{2+} + H_2O(l)$
electrolytes	anolyte: $VSO_4$ solution catholyte: $(VO_2)_2SO_4$ solution
other information about the battery	The technical benefits of this battery include: (a) Separate storage tanks can be used to store the chemical energy. These tanks are separate from the battery. (b) The system is safe because there is less risk of the electrolytes suddenly mixing and releasing energy. (c) The solutions act as coolants as they are pumped through the stack of cells inside the battery. (d) Vanadium solutions are present in both compartments and so contamination is less of a problem. (e) There is a very high-energy efficiency as the electrochemical reactions are readily reversible.
cost and practicality	High cost until fully commercialised. Vanadium is a plentiful metal and this will help to reduce costs. The battery can be recharged at a low voltage (e.g. 2 V) but can deliver a high voltage (e.g. 100 V) on discharge.  Very little explosive hydrogen is generated in recharging, so natural ventilation is sufficient.
effect on society	Some important applications of this technology include: (a) electrochemical storage of solar energy collected by photo-voltaic cells (b) replacement of lead-acid storage batteries used to power-up diesel engines, especially in remote areas; lead-acid storage batteries are durable but present an environmental problem in disposal as lead is a toxic metal (c) electrochemical storage of wind energy collected by wind generators operating in low wind areas; this is made possible because the vanadium battery can be recharged at low voltages, acting as an emergency backup battery system (d) power source for electric vehicles.
effect on the environment	The solutions can be indefinitely recycled and waste is minimised.

### Liquid-junction photovoltaic cells (Gratzel cells)

Solar cells are expected to provide environmentally friendly solutions to our future energy needs. One type of photo-voltaic cell using nanocrystalline semiconductor films coated with organometallic dye molecules is called a Gratzel cell after its discoverer. A network of 10 nm  $TiO_2$  semi-conductor particles (or mixtures of  $TiO_2$ ,  $ZnO$ ,  $Ta_2O_5$  and  $Nb_2O_5$ ) containing pores through which a liquid conductor (redox electrolyte) can flow is the basis of this cell. Light photons are absorbed by a photosensitive ruthenium dye that coats the pores of the solid particles. Electrons become excited within the dye and are then transferred via the  $TiO_2$  into the transparent film of the anode and then into the external circuit. This process causes the dye to be oxidised. The oxidised dye is reduced by iodide ions in the electrolyte and becomes available for further photon absorption. The triiodide ions that form move towards the cathode and are reduced back to iodide ions.

## SYLLABUS FOCUS

Research into these dye-sensitised photovoltaic cells continues. Experiments in the Netherlands have shown that solid CuSCN can be used to replace the iodide-triiodide system in the liquid-junction voltaic cells previously described. In these cells, electron transport occurs in the  $\text{TiO}_2$ , and positive hole transfer occurs in the CuSCN.



**Figure 4.20** Gratzel cells are liquid-junction photovoltaic cells.

**Table 4.9** Chemistry of a typical Gratzel cell

Cell function	Comment
voltage	0.76 volts
anode (-)	glass/transparent metal layer/ $\text{TiO}_2$ semiconductor coated with photo emissive ruthenium dye
anode half-equation	Absorption of light photon causes an electron to be emitted from the ruthenium dye / $\text{TiO}_2$ particle. $\text{Ru(dye)} \rightarrow \text{Ru(dye)}^+ + e^-$
cathode (+)	glass/transparent $\text{SnO}_2$ conducting layer/ Pt catalyst (The cathode is called the <i>counter electrode</i> .)
cathode half-equation	$\text{I}_3^- + 2e^- \rightarrow 3\text{I}^-$
electrolyte	molten mixture of iodide-triiodide ions or dissolved in organic solvent
other information about the battery	The oxidised dye is regenerated back to its reduced state by gaining electrons from the iodide ions present in the electrolyte. $2\text{Ru(dye)}^+ + 3\text{I}^- \rightarrow 2\text{Ru(dye)} + \text{I}_3^-$ The $\text{I}_3^-$ ion is reduced at the cathode.
cost and practicality	High initial expense due to low demand and research costs; $\text{TiO}_2$ and the other oxides are relatively cheap. Only small amounts of expensive platinum are used. These cells are simple to construct.
effect on society	Solar cells constructed using this technology can be used to capture sunlight. They can be constructed as roof and window panels.
effect on the environment	$\text{TiO}_2$ and the other oxides are non-toxic. Silicon solar cell manufacture produces much toxic waste whereas $\text{TiO}_2$ manufacture generates much less waste.

## 4.2 Questions

1. Luigi set up three galvanic cells under standard conditions in the laboratory. He used a lead half-cell containing the  $\text{Pb} | \text{Pb}^{2+}$  couple as the reference standard. This half-cell was always connected to the positive voltmeter terminal in each experiment. Other half-cells were connected in turn with this reference couple. The results of Luigi's experiment are tabulated below:

Cell	Couple 1	Couple 2	Voltage (V)
A	$\text{Cd}   \text{Cd}^{2+}$	$\text{Pb}   \text{Pb}^{2+}$	+0.27
B	$\text{Cu}   \text{Cu}^{2+}$	$\text{Pb}   \text{Pb}^{2+}$	-0.21
C	$\text{Sn}   \text{Sn}^{2+}$	$\text{Pb}   \text{Pb}^{2+}$	+0.01

Luigi examined the results of the experiment. He determined the relative order of reductant strength of these four metals from the results. Use Luigi's data to organise the metals according to their strengths as reductants.

2. Draw the galvanic cell from each of the following cell diagrams. Include a voltmeter in the circuit.
- (a)  $\text{Zn}(\text{s}) | \text{Zn}^{2+} \parallel \text{Cu}^{2+} | \text{Cu}(\text{s})$
  - (b)  $\text{Pt}(\text{s}), \text{H}_2(\text{g}) | \text{H}^+ \parallel \text{Ag}^+ | \text{Ag}(\text{s})$

For each cell:

- (i) show the direction of electron flow in the external circuit
- (ii) label the anode and cathode; indicate whether they are positive or negative
- (iii) write the reduction and oxidation half-equations
- (iv) write the net cell equation.

3. Examine the following net cell equation.



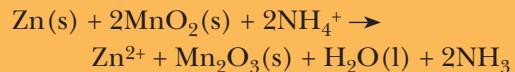
- (a) Draw a labelled galvanic cell indicating the anode and cathode materials.
- (b) Write the oxidation and reduction half-equations.
- (c) State the direction of electron flow in the external circuit.

4. Use the table of standard reduction potentials in Appendix 2 to determine the standard cell potential of the following galvanic cells.

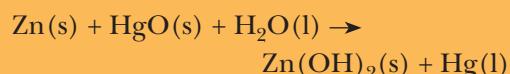


5. Determine the change in oxidation state of the species undergoing reduction in each of the galvanic cells whose cell equation is written below.

(a) Dry cell:



(b) Mercury button cell:



6. In 1974 the first cardiac pacemaker was developed. This corrected arrhythmias in heart muscles. The pacemaker contained a galvanic cell that generated a voltage of 3.5 V. The cell's electrolyte was a solution of lithium chromate ( $\text{Li}_2\text{CrO}_4$ ).

The cell reaction is:



- (a) Identify the species that is undergoing oxidation in this cell.
- (b) (i) Identify the change in oxidation state at the cathode.
- (ii) Explain why the cathode requires the presence of a graphite rod.

7. Button cells are important because of their size and constant voltage. They are commonly used in watches and hearing aids. One type of button cell is the silver oxide–cadmium button cell. The silver oxide–cadmium galvanic cell is an alkaline cell that has a cell voltage of 1.3 V. At the anode, the cadmium in the presence of hydroxide ions is oxidised to form a precipitate of cadmium hydroxide. At the cathode, silver oxide in the presence of water is reduced to silver metal.

Write the:

- (a) anode half-equation
- (b) cathode half-equation
- (c) net cell equation.

8. Explain why a corrosive paste may leak from a Leclanché dry cell.

9. Compare dry cells and silver button cells in terms of their costs, uses, and their impacts on society and the environment.

10. Assess the issues related to the replacement of lead–acid batteries by the vanadium redox battery in motor vehicles.



## SUMMARY

- Reduction is the process of electron gain and oxidation is the process of electron loss in a chemical change.
- Oxidants (such as metal ions) cause the oxidation of reductants (such as metals). Reductants cause the reduction of oxidants.
- Elements in molecules and ions can be assigned oxidation states which assist in determining which species has been oxidised or reduced.
- The relative strengths of oxidants and reductants can be compared by performing simple metal displacement reactions and by constructing simple galvanic cells.
- The electrochemical series lists oxidants and reductants in order of their oxidising and reducing strengths.
- In a galvanic cell, oxidation occurs at the negative electrode (anode) and reduction occurs at the positive electrode (cathode).
- The table of standard electrode potentials is a comparison of reduction potentials of test couples with the standard hydrogen electrode.
- The spontaneity of a redox reaction can be predicted using the table of standard electrode potentials.
- Galvanic cells generate electrical energy from chemical potential energy.
- Batteries can be created by joining several galvanic cells in series.
- Batteries may be non-rechargeable (e.g. dry cell) or rechargeable (lead-acid battery).
- New batteries are being developed. These batteries must be cost effective and environmentally friendly sources of electrical energy.

# PRACTICAL ACTIVITIES

## 4.1 PRACTICAL ACTIVITIES GALVANIC CELLS

### Aim

To perform first-hand investigations in the school laboratory to determine the conditions under which galvanic cells are formed and to measure the difference in voltage of different combinations of metals in electrolyte solutions

### Materials

- 150 mL beakers
- 100 mL measuring cylinder
- DC voltmeter
- porous pot as an ion partition
- U-tube filled with saturated  $\text{KNO}_3$  agar gel
- electrodes (graphite, zinc, nickel, copper and magnesium — electrodes should be free of corrosion)
- electrolytes (0.1 molar solutions of  $\text{NaCl}$ ,  $\text{KNO}_3$ ,  $\text{HNO}_3$ ,  $\text{CuSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{NiSO}_4$  and  $\text{ZnSO}_4$ )
- electrical leads

### Safety

- Wear safety glasses throughout this experiment.
- Identify other safety precautions by reading the method for these experiments.

### Part 1: Experimental investigation — Conditions for galvanic cell formation

Three variables will be investigated in this section:

- effect of electrode material
- effect of different electrolytes
- effect of different electrolyte concentrations.

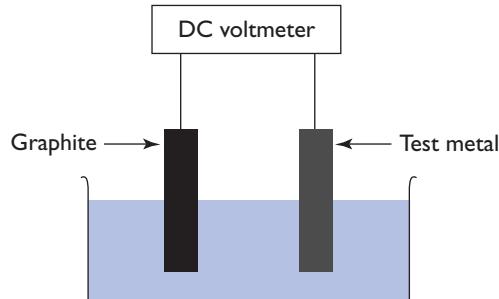
#### Effect of electrode material

The basic apparatus consists of a 150 mL beaker containing 50 mL of 0.1 molar sodium chloride solution. Two electrodes (graphite and the test metal) are placed in the beaker and connected

to a 2 V DC voltmeter. You will measure the potential difference between the graphite and metal electrode. No salt bridge is needed as the electrolytes are the same for each half-cell.

1. In your work groups, discuss how you will be able to control the variables so as to obtain reliable voltage readings. Once you have identified the best way to conduct the experiment, ensure that all tests are done so that the variables are controlled.
2. Measure the potential difference for each cell for each of the following test metals:  
zinc, nickel, copper, magnesium

In each case, record the name of the electrode material connected to the negative voltmeter terminal.



**Figure 4.21** In this simple galvanic cell, only one beaker is used. A potential difference is established as the electrodes are different.

#### Effect of different electrolytes

- The experimental apparatus is the same as in the previous experiment.
- The two electrodes to be used are graphite and zinc.
- The electrolytes to be tested are 0.1 molar solutions of:
  - (a) sodium chloride
  - (b) potassium nitrate
  - (c) nitric acid.

1. In your work groups, discuss any additional issues about variable control so as to ensure accuracy and reliability.
2. Measure the potential difference for each cell. Tabulate your results.

# PRACTICAL ACTIVITIES

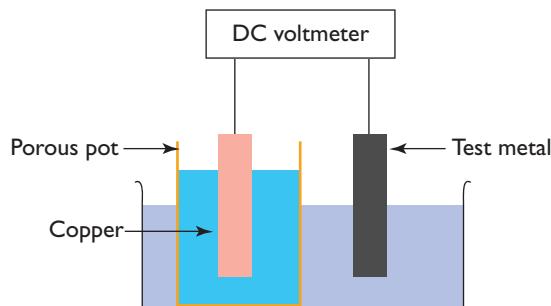
## Effect of different electrolyte concentration

- The experimental apparatus is the same as in the previous experiment.
  - The two electrodes to be used are graphite and zinc.
  - The electrolyte is sodium chloride solution. Its initial concentration is 0.1 molar.
- In your groups, devise a volumetric procedure using a 100 mL measuring cylinder to produce 50 mL samples of sodium chloride solution of the following molarities:  
0.08 mol/L, 0.04 mol/L, 0.02 mol/L,  
0.01 mol/L, 0.005 mol/L.
  - Measure the potential difference for each cell as you vary the concentration of the electrolyte.
  - Tabulate your results.

## Part 2: Experimental investigation — Potential difference of different metal-electrolyte combinations

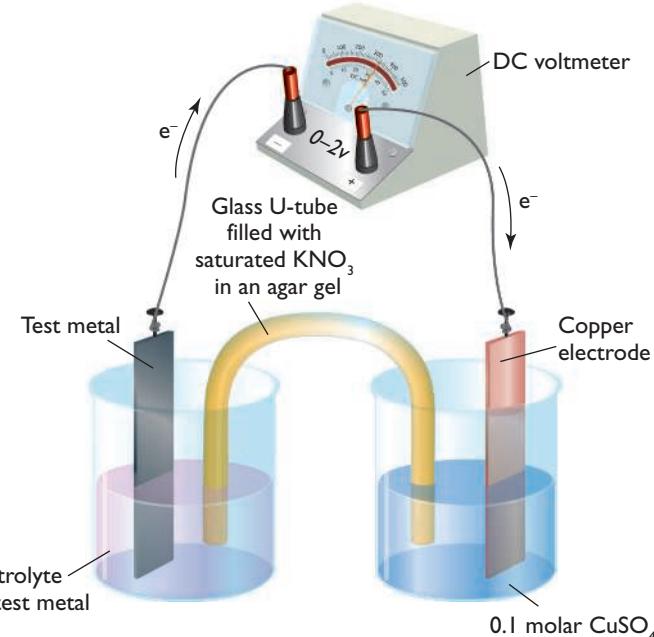
The apparatus for this section consist of two separate half-cells.

In Part A, one half-cell is a 500 mL beaker and the second half-cell is a porous pot that sits inside the beaker. Electrodes dip into each solution and are connected to a DC voltmeter. The porous pot acts as an ion bridge or salt bridge. It has a lower resistance than filter paper soaked in salt.



**Figure 4.22** An unglazed ceramic pot makes an excellent porous partition to separate each half cell.

In Part B, use two 150 mL beakers as the two half-cells and use an inverted U-tube filled with a  $\text{KNO}_3$  agar gel as an ion bridge. Ensure no air bubbles are caught at the tips of the U-tube when it is inverted.



**Figure 4.23** A gel of potassium nitrate solution and agar makes a very good ion bridge as long as no air bubbles are present.

### Part A

- The 0.1 molar copper (II) sulfate solution is placed in the porous pot. A copper electrode completes this half-cell. This is the reference couple:  $\text{Cu} \mid \text{CuSO}_4$   
The beaker contains the test couple. Use only enough solution to make electrical contact.  
There is no need to fill the beakers.
- The test couples are:



- Measure the potential difference between each test couple and the reference couple.  
Note the couple that is connected to the negative voltmeter terminal. Tabulate your results.

### Part B

- Set up the two beakers and the U-tube ion bridge as shown in Figure 4.11.
- One beaker is the copper reference couple. The other beaker is one of the test couples.
- Repeat the measurements made in Part A and record the voltages obtained.

# PRACTICAL ACTIVITIES

## Results, analysis and discussion

1. Summarise and discuss the effects of the different variables on the potential difference of galvanic cells.
2. Discuss the results of the experiments involving the measurement of the potential difference between test couples and a copper reference couple. Relate your observation to the activity series of metals.
3. (a) Use a table of standard electrode potentials to calculate the cell potential for each cell investigated in Part 2. In each case write both half-equations and the net cell equation.  
(b) Account for any differences between the calculated cell potentials and those measured in Part 2 of your experiment. Identify which ion bridge gave more accurate results.
4. Summarise the issues that you identified in your groups that will improve accuracy and reliability of the experimental results (Part 1).

# DATA ANALYSIS

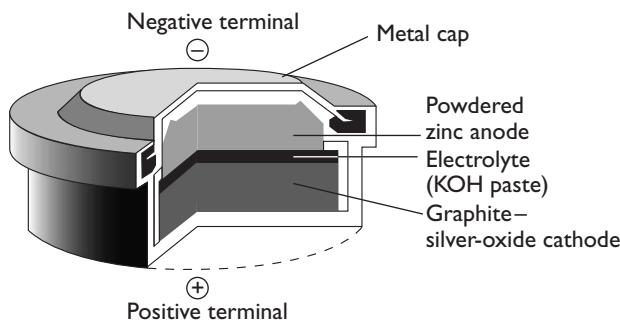
## 4.2 DATA ANALYSIS

### COMPARING BATTERIES

The following information will allow you to compare a button cell and a fuel cell with the dry cell and the lead–acid battery. Read the information and then answer the questions that follow.

#### Battery A — the silver button cell

The button cell was developed for appliances that required small cells with stable voltages during operation.



**Figure 4.24** The silver button cell is widely used in watches, hearing aids and cameras.

**Table 4.10** Chemistry of the silver button cell

Cell feature	Comment
voltage	1.6 volts
anode (-)	zinc
anode half-equation	$\text{Zn}(\text{s}) + 2\text{OH}^- \rightarrow \text{Zn}(\text{OH})_2(\text{s}) + 2\text{e}^-$
cathode (+)	C (graphite) + silver oxide paste
cathode half-equation	$\text{Ag}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow 2\text{Ag}(\text{s}) + 2\text{OH}^-$
electrolyte	KOH paste plus some dissolved zinc hydroxide in a porous carrier.
other information about the battery	The powdered anode (large surface area) provides a high current density over a long time. The metallic silver produced by the cathode half-reaction assists the conductivity of the cell. The constant hydroxide ion concentration helps to maintain a stable voltage.

cost and practicality	Cells are expensive due to the high cost of silver; it is non-rechargeable and so it should be recycled rather than discarded so that the silver can be recovered. It has a long shelf life.
effect on society	They are widely used in watches, cameras, hearing aids or other appliances that require a small battery that produces a stable voltage over the battery's life.
effect on the environment	None of the materials are toxic although the KOH is highly caustic and can cause burns if the battery is damaged.

#### Questions

In this set of questions we will compare the silver button cell to the dry cell.

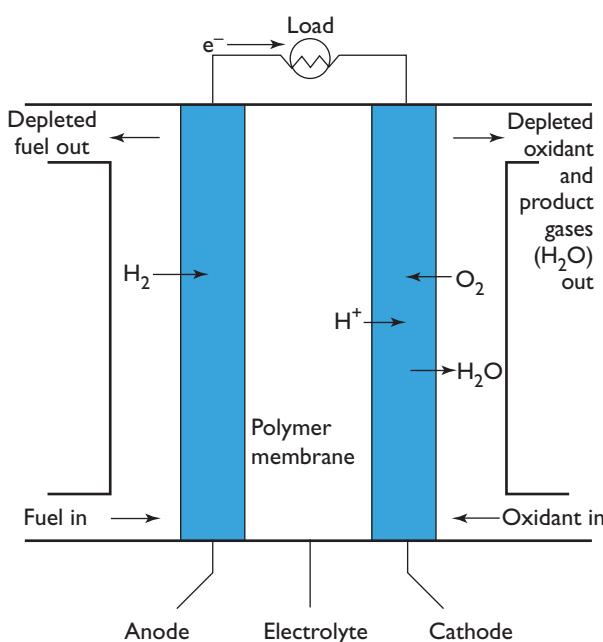
- State the similarities between the silver button cell and the dry cell in terms of their chemistry.
- State the differences between the silver button cell and the dry cell in terms of their chemistry.
- Identify which cell:
  - is cheaper to purchase
  - produces a more stable voltage over the life of the cell
  - is more suited to use in small appliances
  - produces a higher current density
  - should be recycled.
- Write the net cell reaction for the dry cell and the silver button cell.
- Use the method of oxidation states to determine which species have been oxidised and reduced in the net cell equation for each cell.

#### Battery B — oxygen–hydrogen fuel cell (PEMFC)

Fuel cells are galvanic cells in which the fuel (the reductant) and the oxidiser (the oxidant) are constantly replenished from a reservoir outside the cell. They were not fully developed until the Gemini and Apollo space missions of the 1960s and 1970s. These early cells used alkaline hydrogen–oxygen fuel cells operating at 250°C to power the command modules. The ill-fated Apollo 13 mission in April 1970 used three such cells, which were disabled after an explosion on the outward journey to the Moon. The crew then relied

# DATA ANALYSIS

on non-rechargeable batteries in the lunar module to provide electrical energy for the return journey. More modern technology has led to proton exchange membrane fuel cells (PEMFC) that operate at much lower temperatures (80–85°C).



**Figure 4.25** The proton exchange membrane fuel cell (PEMFC) offers higher power density than many other fuel cells. The use of a solid polymer electrolyte eliminates corrosion and safety concerns associated with liquid electrolyte fuel cells. It has a low operating temperature and provides instant start-up.

**Table 4.11** Chemistry of a proton exchange membrane fuel cell

Cell feature	Comment
voltage	0.7 volts
anode (-)	platinum catalyst on graphite-coated, ridged paper
anode half-equation	H <sub>2</sub> (g) → 2H <sup>+</sup> + 2e <sup>-</sup>
cathode (+)	platinum catalyst on graphite-coated, ridged paper
cathode half-equation	O <sub>2</sub> (g) + 4H <sup>+</sup> + 4e <sup>-</sup> → 2H <sub>2</sub> O(l)
electrolyte	fluorocarbon polymer with sulfonic acid functional groups; the membrane provides a conducting path for the hydrogen ions (protons).

other information about the battery	The water produced by the cell reaction is ejected in the oxidant gas flow. Pure hydrogen must be used, otherwise the platinum catalyst is deactivated.
cost and practicality	High cost due to the high developmental costs; only a little thermal shielding is required to protect personnel as the cell operates at 85°C. This cell could be ideal for commercial applications.
effect on society	There is not likely to be a short-term impact as this is a developing technology. The long operating lifetime (in excess of 50 000 hours) is impressive. This cell may be one of the technologies that eventually replace the fossil fuel energy sources. The cell has instant start-up.
effect on the environment	In the long term, such a cell that utilises non-fossil fuels may be an important power source. The water that is produced is a non-pollutant. Because the cell uses hydrogen, storage may be a risk. No toxic materials are used.

## Questions

In this set of questions we compare the PEMFC to the lead-acid storage battery.

- State the similarities between the proton exchange fuel cell and the lead-acid battery in terms of their chemistry.
- State the differences between the proton exchange fuel cell and the lead-acid battery in terms of their chemistry.
- Identify which cell or battery:
  - is currently cheaper to manufacture
  - does not produce pollutants during its operation
  - requires cooling during its operation
  - has a highly conductive liquid electrolyte.
- Write the net cell reaction for the PEMFC and explain why the cell is called a fuel cell.
- Explain how the lead-acid battery and the PEMFC can be recharged.