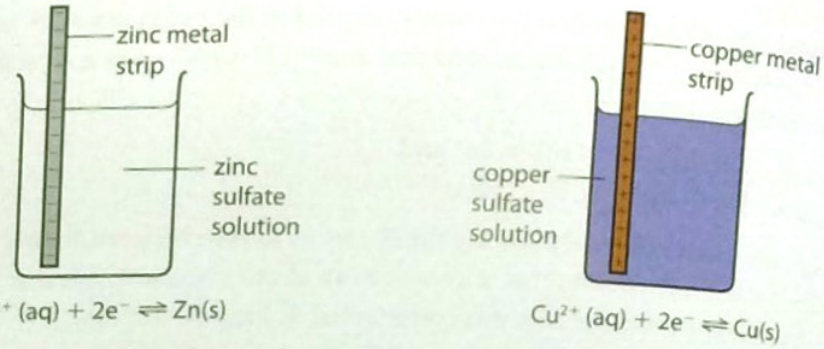


Figure 9.4 The zinc half cell develops a negative potential with respect to the copper half cell.

Some zinc atoms from the metal strip release electrons, giving it a negative charge.

Some copper ions in the solution accept electrons from the copper rod giving a positive charge

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

Two connected half cells make a voltaic cell

If we now connect these two half cells by an external wire, electrons will have a tendency to flow spontaneously from the zinc half cell to the copper half cell because of their different electrode potentials. The half cells connected in this way are often called **electrodes** and their name gives us information about the type of reaction that occurs there. The electrode where oxidation occurs is called the **anode**, in this case it is the zinc electrode:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \quad \text{and it has a negative charge.}$$

The electrode where reduction occurs is called the **cathode**, in this case it is the copper electrode:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad \text{and it has a positive charge.}$$

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

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

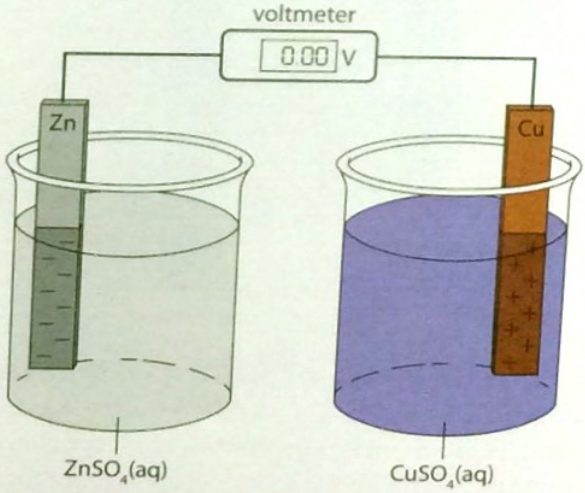


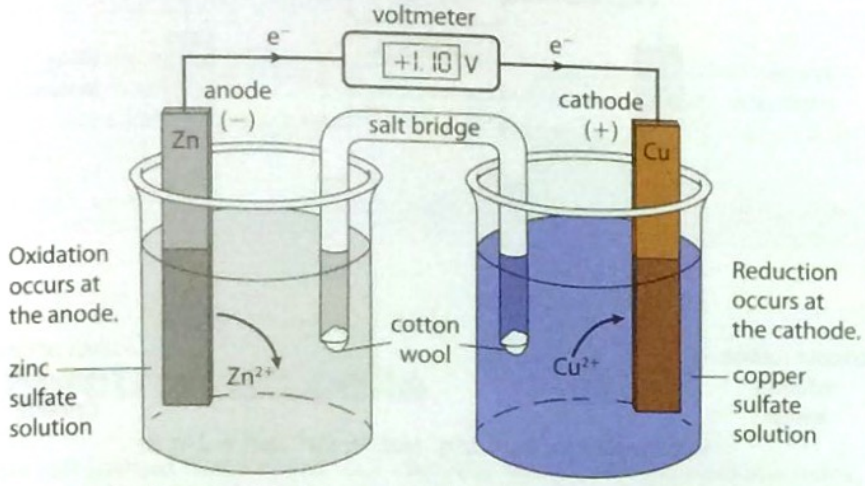
Figure 9.5 This cell has an incomplete circuit – no voltage is generated. A salt bridge must be added to allow ions to flow between the two electrodes.

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

The voltaic cell therefore must have the following connections between the half cells:

- An electrical wire, connected to the metal electrode in each half cell. A voltmeter can also be attached to this external circuit to record the voltage generated. Electrons will flow from the anode to the cathode through the wire.
- A salt bridge that completes the circuit. The salt bridge is a glass tube or strip of absorptive paper that contains an aqueous solution of ions that enables

negative charge to be carried in the opposite direction to that of the electrons (from cathode to anode). This ion movement will neutralize any build up of charge and maintain the potential difference. The solution chosen is often $NaNO_3$ or KNO_3 as these will not interfere with the reactions at the electrodes. Without a salt bridge no voltage will be generated.



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

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

Figure 9.6 A copper–zinc voltaic cell.

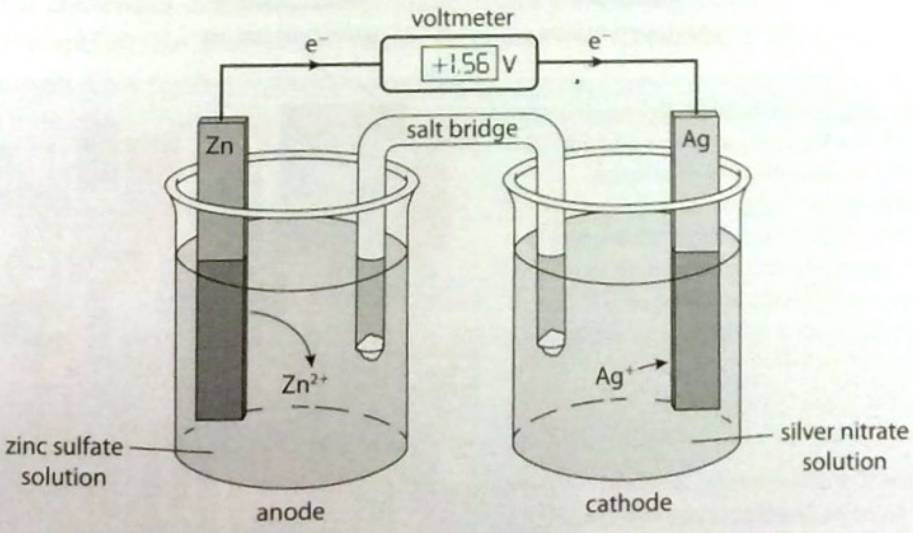
W You can view a simulation of this voltaic cell.
Now go to www.heinemann.co.uk/hotlinks, insert the express code 4259P and click on this activity.

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

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

Different half cells make voltaic cells with different voltages

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



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

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

Figure 9.7 A silver–zinc voltaic cell.

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

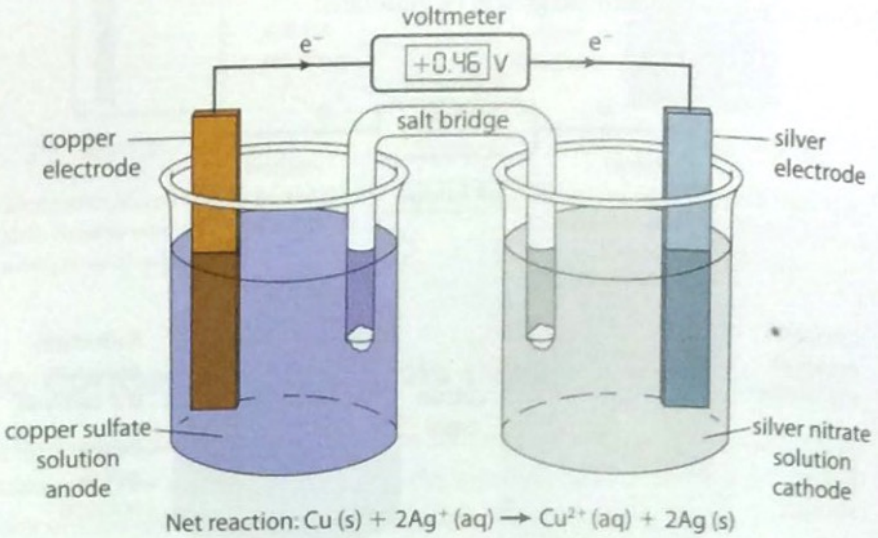


Figure 9.8 A silver–copper voltaic cell.

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

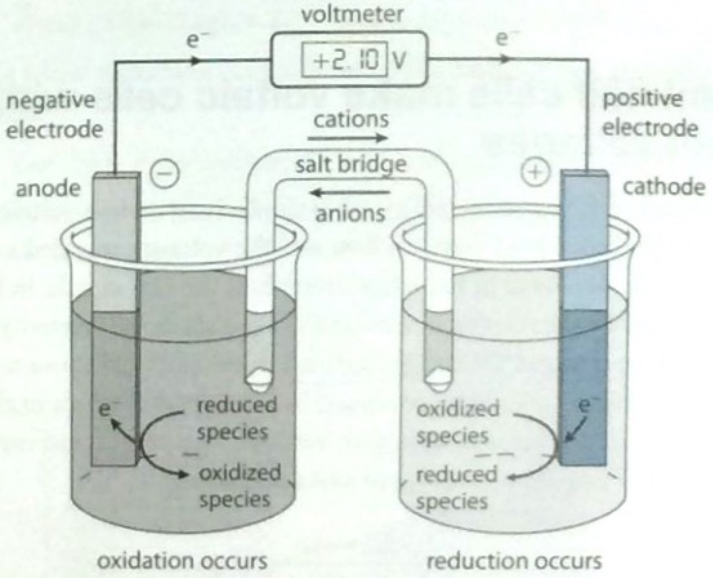


Figure 9.9 Summary of the components of a voltaic cell showing the ion and electron movements.

You can simulate different voltaic cells and see the effect of changing conditions.
Now go to www.heinemann.co.uk/hotlinks, insert the express code 4259P and click on this activity.

Batteries are an application of a voltaic cell, making electrical energy available as a source of power. Our reliance on batteries increases as we develop more and more portable energy-hungry electronic devices such as camera phones and high performance portable computers. The global market for batteries is over 60 billion US dollars and rising sharply, especially in China, India, Brazil, Czech Republic and South Korea. While demand for batteries looks set to continue, concern over toxicity and environmental damage from battery disposal has meant that mercury and cadmium batteries are being phased out in many places. The different types of batteries and their relative advantages are explained more fully in Option C, Chapter 14.

An assortment of different types, sizes and brands of batteries. The output and effective life of a battery depends on which chemicals it uses to produce the electric current.

Exercises

8 Use the metal reactivity series given earlier to predict which electrode will be the anode and which will be the cathode when the following half cells are connected. Write half equations for the reactions occurring at each electrode.

(a) Zn/Zn^{2+} and Fe/Fe^{2+}

(b) Fe/Fe^{2+} and Mg/Mg^{2+}

(c) Mg/Mg^{2+} and Cu/Cu^{2+}

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

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

9.5 Electrolytic cells

We have just learned that a voltaic cell takes the energy of a spontaneous redox reaction and harnesses it to produce electric voltage. An electrolytic cell does the reverse: it uses an external source of voltage to bring about a redox reaction that would otherwise be non-spontaneous. You can think of it in terms of an external power supply effectively pumping electrons into the electrolytic cell, driving redox reactions. As a result, electrolysis enables neutral elements to be released from ionic compounds, by **discharging** the ions (removing their charge) through oxidation and reduction reactions. This is why it is such an important large-scale process in industry, used in the manufacture of many chemicals.

An electrolytic cell has the following components:

- The source of electric power, for example a battery or a dc power source. This is always shown in diagrams as ||| where the longer line represents the positive terminal and the shorter line the negative terminal.
- The **electrolyte**. This is a liquid that conducts electricity and undergoes chemical change as a result. Electrolytes are commonly molten ionic compounds, or aqueous solutions of ionic compounds.
- The **electrodes**. These are always made from a conducting substance (a metal or graphite) that is immersed in the electrolyte and connected to the power supply. They must not touch each other!
- Electrical conductors (wires) to connect the power supply to the electrodes.

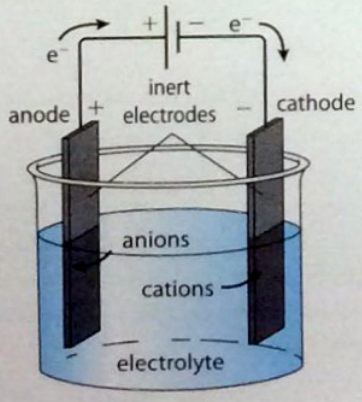


Figure 9.10 Components of an electrolytic cell.

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

You can read Michael Faraday's paper 'On electrical decomposition'.
Now go to www.heinemann.co.uk/hotlinks, insert the express code 4259P and click on this activity.

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

Conduction of the current through the electrolytic cell

The power source pushes electrons towards the negative electrode where they enter the electrolyte. They are released at the positive terminal and returned to the source. The current is passed through the electrolyte by the ions as they migrate to the electrodes.

Redox reactions occur at the electrodes

The ions in the electrolyte migrate to the electrodes by the attraction of opposite charges. The negative electrode attracts positive ions (cations) while the positive electrode attracts negative ions (anions). At the electrodes redox reactions occur which result in the ions being discharged and released as neutral products.

At the negative electrode (cathode): $M^+ + e^- \rightarrow M$

Cations gain electrons and so are reduced.

At the positive electrode (anode): $A^- \rightarrow A + e^-$

Anions lose electrons and so are oxidized.

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

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

You can view a simulation of electrolytic cells.
Now go to heinemann.co.uk/hotlinks, insert the express code 4259P and click on this activity.

	Voltaic cell		Electrolytic cell	
anode	oxidation occurs here	negative	oxidation occurs here	positive
cathode	reduction occurs here	positive	reduction occurs here	negative

Knowing the chemical nature of the electrolyte enables us to deduce the electrode reactions that will occur and hence the products that will be released from the electrolytic cell.

Electrolysis of molten NaCl

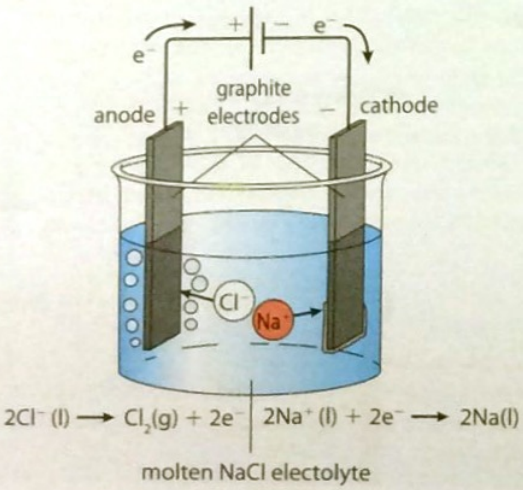


Figure 9.11 Electrolysis of molten sodium chloride.

Worked example

Write half equations for the electrode reactions that occur when molten NaCl is electrolysed.

Solution

(a) Deduce the ions present and to which electrode they will be attracted.

$$NaCl \rightarrow Na^+ \text{ and } Cl^-$$

$$\downarrow \qquad \downarrow$$

to cathode to anode

(b) Write half equations for the reactions in which these ions will be discharged at each electrode and what might be observed.

At the anode: oxidation:

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

We know that Cl atoms will combine to make Cl_2 as this is the most stable form of chlorine.

At the cathode: reduction:

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

In the cell there must be an equal number of electrons released at the anode as are taken up at the cathode, so here we need to double the equation at the cathode:

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

So a pale green gas will collect around the anode and a metallic liquid (at the temperature of this cell) will form at the cathode.

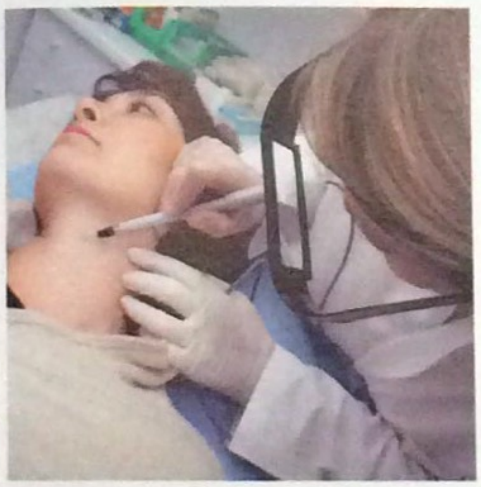
Overall reaction: $2NaCl(l) \rightarrow 2Na(l) + Cl_2(g)$

Electroplating is a process using electrolysis to deposit a layer of one metal on top of another metal. This is done to cover a metal with a decorative, more expensive or corrosion-resistant layer of another metal. For example, silver plating a spoon uses a silver anode and an iron spoon cathode. Galvanizing iron involves depositing a layer of zinc on top of the iron to help protect it from corrosion as the zinc will be preferentially oxidized. This is sometimes called sacrificial protection.

Exercise

11 Write half equations for the electrode reactions occurring during the electrolysis of the following molten salts:

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



Electrolysis is used to remove unwanted hairs permanently. The needle is inserted into the hair shaft and passes an electric current through the follicle. Electrolytic reactions result in the production of NaOH, which destroys the hair follicle.

Technician inspecting components that have been electroplated with chromium. The process used an electrolytic cell containing chromium ions in the electrolyte which were reduced and deposited at the cathode, which was made of the components to be coated.

Aluminium is a unique metal: strong, flexible, lightweight, corrosion resistant and 100% recyclable. Its commercial manufacture began in the 1880s when electrolysis made it possible to extract it from its ore, bauxite, Al_2O_3. It is therefore a young metal in contrast to tin, lead and iron which have been in use for thousands of years, but in this short time it has become the world's second most used metal after steel. Aluminium production is, however, very energy intensive and also is associated with the production of perfluorocarbons (PFCs), strong greenhouse gases. A major emphasis must therefore be placed on recycling the metal as this uses only 5% of the energy and has only 5% of the greenhouse gas emissions compared with aluminium production. Recycling of old scrap now saves an estimated 84 million tonnes of greenhouse gas emissions per year.

The aluminium drink can is the world's most recycled container. More than 63% of all cans are recycled worldwide.