Extension 7: Electrolysis

1. Prerequisites

The key ideas required to understand this section are:

Topic	Book page
Redox reactions	102
Writing and balancing redox equations	106
Standard electrode potentials	109
The mole and Avogadro's constant	122

2. Electrolysis

Ionic compounds, molten or in aqueous solution, will conduct electricity. The solution (or melt) is called an **electrolyte**. Electrolytes undergo chemical change (**electrolysis**) when they conduct; the electrolyte 'splits up' into simpler substances. In order to pass electricity into an electrolyte, rods of metal or carbon (**electrodes**), connected to a battery, are dipped into the liquid. The electrode connected to the negative terminal of the battery is the **cathode**, while that connected to the positive terminal is the **anode**. (See Fig. 7.1).

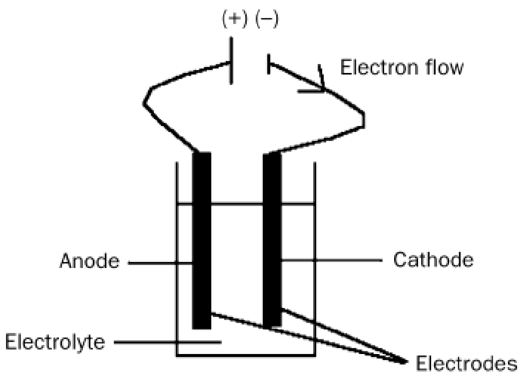


Fig. 7.1 Electrolysis

3. The electrolysis of molten sodium chloride

In the electrolysis of molten sodium chloride (which melts at 801°C), sodium ions (Na^+) and chloride ions (Cl^-) are free to move around in the melt. Carbon electrodes, connected to a battery, are dipped into the melt. The cathode, because it is negatively charged, attracts the positive ions from the melt, where the ions receive electrons supplied by the battery (the ions are discharged). Sodium atoms are formed and molten sodium metal forms at the cathode:

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

The anode attracts the negatively charged Cl^- ions, where they each give up one electron. The electrons go into the anode and pass back along the wire to the battery. In this way, the circuit is completed.

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

Chlorine atoms join together to form diatomic molecules:

$$Cl + Cl \rightarrow Cl_{2(g)}$$

Note that these two stages are usually written as one half-reaction:

$$2Cl^{-}_{(l)} \rightarrow Cl_{2(g)} + 2e^{-}$$

Therefore, sodium metal is formed at the cathode and bubbles of chlorine gas form at the anode. Chemical changes take place at both electrodes, sodium ions are reduced and chloride ions are oxidized. Electrons do not actually pass through the liquid, but an equal number of electrons are given up at the cathode as are received at the anode.

The overall chemical equation for the reactions that take place is:

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

EXERCISE **7A**

The electrolysis of molten lead bromide

1. Potassium iodide, KI, contains potassium ions (K^+) and iodide ions (I^-).
- **(i)** Write equations for the reactions that occur at the anode and cathode when molten potassium iodide is electrolysed.
- **(ii)** Write an overall equation for the reaction.

2. Lead iodide, $PbBr_2$, contains lead ions (Pb^{2+}) and bromide ions (Br^-).
- **(i)** Write equations for the reactions that occur at the anode and cathode when molten lead bromide is electrolyzed.
- **(ii)** Write an overall equation for the reaction.

4. The electrolysis of aqueous sodium chloride

If electrolysis is carried out in aqueous solution, the situation is much more complicated. Water contains covalently bonded molecules, but a small proportion of these molecules split up into ions:

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

In a solution of a salt, such as sodium chloride solution, four different ions will be present: $Na^+(aq)$, $Cl^-(aq)$, $H_3O^+(aq)$ and $OH^-(aq)$. When the solution is electrolyzed, the cations $Na^+(aq)$ and $H_3O^+(aq)$ will be attracted to the negatively charged cathode, whilst $Cl^-(aq)$ and $OH^-(aq)$ will be attracted to the positively charged anode. One type of ion is discharged, in preference to the other, at each electrode. In general, the ion that is discharged depends upon:

(i) The material that is in the electrodes.
(ii) The concentration of the ions present in solution.
(iii) E^θ for the half reaction in solution.

If a concentrated solution of sodium chloride (brine) is electrolyzed, using graphite or platinum electrodes, hydronium ions accept electrons at the cathode and bubbles of hydrogen appear:

$$2H_3O^+(aq) + 2e^- \rightarrow H_2(g) + 2H_2O(l)$$

This might also be written:

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

Hydrogen ions are discharged instead of sodium ions because they accept electrons more readily (compare their E^θ values). Chloride ions are discharged at the anode because they are present in a high concentration. Chlorine gas is formed:

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

The outcome of the electrolysis of *aqueous* sodium chloride is therefore different from that of the molten salt.

EXERCISE **7B**

The electrolysis of aqueous sodium chloride

(i) What ions are left in solution when aqueous sodium chloride is electrolyzed?

(ii) The solution of sodium chloride is neutral before electrolysis. Does it remain neutral?

5. Uses of electrolysis

The electrolysis of brine

On an industrial scale, the electrolysis of brine is used for the production of:

- Hydrogen – used as fuel;
- Chlorine – used as a bleach and disinfectant;
- Sodium hydroxide – this has many uses, including in the making of soaps and detergents.

Purification

Electrolysis is used to purify copper metal. When an aqueous solution of copper sulphate is electrolyzed using **copper** electrodes, the following reactions occur:

- The copper of the anode ionizes and dissolves into the solution. The impurities in the anode drop to the bottom of the container.

  $$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$$
- Copper ions in the solution gain electrons at the cathode and copper metal is deposited on the cathode.

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

  The process is shown in Fig. 7.2.

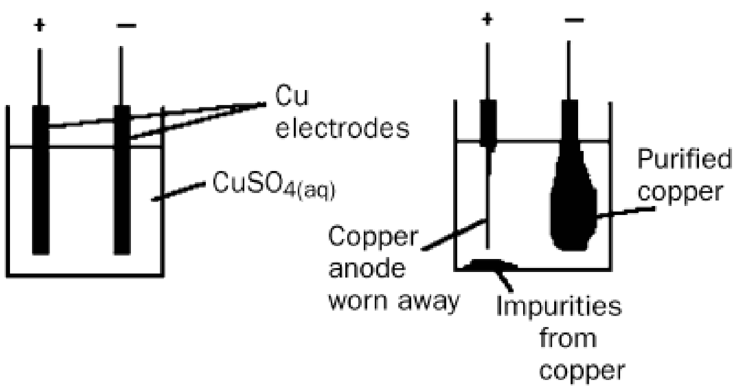


Fig. 7.2 Purifying copper

Electroplating

Electrolysis can be used to coat one metal with another or **electroplate** metals. If, in Fig. 7.2, the cathode had been made from a metal other than copper, it would still have become coated with a layer of copper.

Silver plating is generally carried out in order to make metal objects look more attractive. The process is the same as that in Fig. 7.2, except that:

- A silver anode is used.
- The metal object to be plated is used as the cathode.
- The anode and cathode are dipped into a solution containing silver ions; for example, $AgNO_3(aq)$.

EXERCISE **7C**

Electroplating

Write equations for the reactions that occur at the anode and cathode when a metal object is electroplated with silver.

Extraction of metals

Metals are generally found in nature in the form of their **ores**. An ore is a metalcontaining compound found in rocks. Often, the metal is found in the form of its oxide or sulfide. A chemical reaction is usually needed to break down the ore and produce the metal; the type of chemical reaction used can be related to the position of the metal in the activity series – **the more reactive the metal, the more difficult it is to extract it from its compounds**.

K, Ca, Na, Mg, Al

These metals are very reactive and difficult to isolate from their compounds. **Electrolysis of the molten salt** is the usual method of preparation. Aluminium, for example, is prepared by electrolysis of molten bauxite (Al_2O_3, containing Al^{3+} ions and O^{2-} ions). The key reaction that occurs at the cathode is:

$$Al^{3+}(l) + 3e \rightarrow Al(l)$$

Zn, Fe, Pb

These elements can be produced from their oxides by heating with carbon or carbon monoxide, which are good reducing agents. Iron, for example, is produced by reduction of iron (III) oxide by CO in the blast furnace at a high temperature (around 700°C):

EXERCISE **7D**

The extraction of metals

(i) Aluminium was hardly used before the twentieth century, despite the fact that its ore occurs very abundantly in the Earth's crust. Can you suggest why?

(ii) Aluminium is an expensive metal (compared with, say, iron). Suggest a reason for this.

(iii) The Thermite reaction uses aluminium metal to reduce iron (III) oxide to iron:

$$2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(s)$$

The reaction is highly exothermic and has been used to weld iron into joints between railway tracks. Explain why copper metal cannot be used instead of aluminium.

EXERCISE **7D**

(iv) Magnesium is prepared by the electrolysis of molten $MgCl_2$. Give half-reaction equations for the chemical reactions that occur at the anode and cathode during this process.

(v) Hydrogen gas can be used instead of carbon or carbon monoxide to reduce the tungsten oxide, WO_3, to tungsten metal. Give one disadvantage of using hydrogen gas as a reducing agent.

Cu

Copper is generally found in nature as copper (I) sulphide, Cu_2S. If the sulphide is roasted in air, copper is formed:

$$Cu_2S(s) + O_2(g) \rightarrow 2Cu(l) + SO_2(g)$$

Ag, Au

Found *native* (as the free element), because they are such unreactive elements.

6. The Faraday constant

When an element is produced at the anode or cathode, during electrolysis, the number of moles of the element produced depends upon:

(i) The size of the current passing through the solution or melt.
(ii) The time the current is passed through the system.
(iii) The charge on an ion of the element.

The unit of charge is called the **coulomb** (C). One coulomb is the quantity of electricity passed when a current of one amp is passed for one second. The quantity of electricity can be calculated from the equation:

Quantity of electricity (in coulombs) = current (in amps) × time (in seconds)

If a current of 0.5 amp is passed through a solution of copper sulphate for 10 minutes, the total number of coulombs passed is:

$= 0.5 \times (10 \times 60)$
$= 300$ C

If the same current is passed through the solution for 20 minutes, the total number of coulombs passed:

$= 0.5 \times (20 \times 60)$

$= 600$ C

For the same ion (in this case Cu^{2+}), the amount of copper deposited is directly proportional to the number of coulombs passed; in other words, twice as much copper is discharged at the cathode when 600 C are passed than when 300 C are passed. If 900 C of electricity were passed through the solution, then three times as much copper would be discharged, and so on.

If the same quantity of electricity is passed through different solutions containing ions of different elements, then the relative number of moles of each ion discharged depends upon the charge on the ions. When hydrogen ions are discharged, the process can be written:

$$H^+ + e \rightarrow H$$

If one mole of hydrogen ions are discharged, how many electrons would be needed? From the equation, 1 mol of H^+ needs 1 mol of electrons to be discharged. What is the charge on 1 mol of electrons?

- The magnitude of the charge on a single electron is 1.602177×10^{-19} C
- The magnitude of the charge per mole of electrons is called **Faraday's constant** (*F*).

This is:

the charge on a single electron $\times N_A$ $= 1.602 \times 10^{-19} \times 6.022 \times 10^{23}$
$= 9.647 \times 10^4$

Therefore, Faraday's constant = 9.647×10^4 C mol^{-1}

Faraday's constant is often quoted as 96 500 C mol^{-1}

Generally:

$$\text{amount in mol of atoms of an element discharged} = \frac{\text{amount in mol of electrons passed}}{\text{number of charges on each ion of the element discharged}}$$

EXAMPLE 1

What mass of copper is produced at the cathode when 3.20 amps of current are passed through a solution of copper(II) sulphate for 30 minutes?

Answer

The number of coulombs passed is given by:

Coulombs = amps × time (in seconds)
= 3.20 × 30 × 60 = 5760 C

This corresponds to moles of electrons:

Amount in mol of electrons = $\frac{5760}{96500}$ = 5.97×10^{-2} mol

Since Cu2+ has a charge of 2+, the number of mol of Cu discharged is:

$\frac{5.97 \times 10^{-2}}{2}$ = 2.99×10^{-2} mol

Therefore, the mass of copper discharged = $2.99 \times 10^{-2} \times 63.5 = 1.89$ g

EXERCISE 7E

(use F = 96500 C mol^{-1})

(i) In the electrolysis of salt water, the following processes occur at the anode: How many moles of hydrogen gas are made when 0.5 A is run through the solution for 30 mins?

(ii) For what length of time would a current of 2.0 A need to be applied in order to deposit 10 g of copper metal on an iron object?

(iii) A current is applied to the electrolysis of brine (salt solution) for 3.00 h. During this time, 1 kg of chlorine gas (Cl_2) is generated. What average current flows?

(iv) Cu^{2+} ions are discharged to make Cu. What mass of Cu is made if a 20 A current is used continuously for 1.0 h?

(v) Sodium is deposited at the cathode in the electrolysis of fused salt:

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

What mass of sodium is made if a current of 10 A is passed through the excess of the molten salt for 10 mins?

BOX 1: Michael Faraday

Michael Faraday (1791-1867) was the son of a blacksmith. He was, for the most part, self-educated, and after attending a lecture by Sir Humphry Davy, applied for a job in the eminent scientist's laboratory. He got the job.

He did a great deal of work studying electricity and magnetism. Faraday passed electric current through solutions and found that the current caused a chemical reaction, or electrolysis; he also found that there was a relationship between the amount of current passed through a solution and the amount of product formed at the electrode. His laws of electrolysis were formulated in 1834.

Faraday also succeeded in liquefying a number of gases, including chlorine. He worked on the chemistry of steel and discovered benzene. He initiated the tradition of scientific Christmas lectures for children at the Royal Institute, a practice that has continued into the twenty-first century.

Revision questions

1. Using the oxidation number method, identify the following changes as either oxidation or reduction:

(i) $S^{2-} \rightarrow SO_4^{2-}$

(ii) $CH_4 \rightarrow CO_2$

(iii) $NO_3^- \rightarrow NH_3$

(iv) $P_4 \rightarrow H_3PO_4$

(v) $ClO_2^- \rightarrow Cl_2$

2. Seawater contains sodium bromide and the element bromine can be extracted by treating the seawater with chlorine gas:

$$2NaBr(aq) + Cl_2(g) \rightarrow 2NaCl(aq) + Br_2(aq)$$

Using the oxidation number method, determine which element is oxidized and which element is reduced.

3. The metal cobalt reacts with nitric acid to form aqueous cobalt (III) ions and nitrogen dioxide gas. Write a balanced overall redox equation for the reaction.

4. Consider the following table and answer the accompanying questions:

Reduction half-reaction	E^{θ} **at 25°C/V**
$Cl_2(aq) + 2e^- \rightarrow 2Cl^-_{(aq)}$	+1.36
$Br_2(l) + 2e^- \rightarrow 2Br^-_{(aq)}$	+1.09
$Hg^{2+}(aq) + 2e^- \rightarrow Hg(l)$	+0.85
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	-0.14
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	-1.66

(i) Which element is the strongest reducing agent?
(ii) Which element is the weakest oxidising agent?
(iii) Which is the least reactive metal?
(iv) Will hydrogen gas be given off if tin is added to dilute hydrochloric acid?
(v) Can aluminium metal be oxidized by bromine?
(vi) Can Hg(l) reduce $Al^{3+}(aq)$ to Al(s)?

5. When an aqueous solution of sodium hydroxide is electrolyzed using platinum electrodes, hydrogen is produced at the cathode and oxygen is produced at the anode.
(i) What ions are present in the solution?
(ii) Write redox half-reactions to show what happens at the anode and cathode.
(iii) The liquid around the anode gradually becomes less basic. Explain why.

6.
(i) A current of 0.2 amp was passed through molten potassium chloride for 1 h. What mass of potassium was liberated at the cathode?
(ii) If the same amount of current was passed through molten aluminium oxide for the same time, what mass of aluminium would be liberated at the cathode?

Answers

Exercises

Exercise 7A

1.
(i) $K^+(l) + e^- \rightarrow K(l)$
$2I^-(l) \rightarrow I_2(g) + 2e^-$
(ii) $2K\ I(l) \rightarrow 2K(l) + I_2(g)$

2.
(i) $Pb^{2+}(l) + 2e^- \rightarrow Pb(l)$
$2Br^-\ (l) \rightarrow Br_2(g) + 2e^-$
(ii) $PbBr_2(l) \rightarrow Pb(l) + Br_2(g)$

Exercise 7B

(i) Na^+, OH^-.
(ii) The solution becomes alkaline (NaOH is a strong alkali).

Exercise 7C

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

Exercise 7D

- **(i)** It is extracted from bauxite by electrolysis, and the process requires *electricity*.
- **(ii)** Aluminium oxide (bauxite) is an ionic substance which has a high melting point. Melting the compound requires a great deal of energy (= electricity) and this is the first step in the extraction of aluminium.
- **(iii)** Copper cannot reduce iron (III) oxide to iron, because copper is a less reactive metal than iron.
- **(iv)** Anode: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$.
  Cathode: $Mg^{2+}(l) + 2e^- \rightarrow Mg(l)$.
- **(v)** Hydrogen forms an explosive mixture with oxygen of the air – large-scale use of the gas might prove dangerous!

Exercise 7E

- **(i)** 0.0047 mol.
- **(ii)** 4.2 h.
- **(iii)** 252 A.
- **(iv)** 24 g.
- **(v)** 1.4 g.

Revision questions

1.

- **(i)** Oxidation: sulphur changes oxidation number from -2 to +6.
- **(ii)** Oxidation: carbon changes from -4 to +4.
- **(iii)** Reduction: nitrogen changes from +5 to -3.
- **(iv)** Oxidation: phosphorus changes from 0 to +5.
- **(v)** Reduction: chlorine changes from +3 to 0.

2. Bromine is oxidized; its oxidation number changes from -1 to 0. Chlorine is reduced; its oxidation number changes from 0 to -1.

3. The half-reactions are:

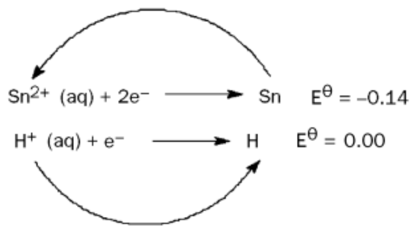
$Co \rightarrow Co^{3+} + 3e^-$ (oxidation)

$NO_3 + 2H^+ + e^- \rightarrow NO_2 + H_2O$ (reduction)

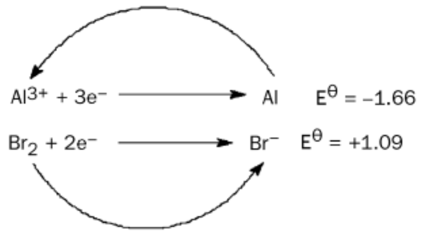
Multiplying the oxidation reaction by 3 and adding: $Co + 3NO_3^- + 6H^+ \rightarrow Co^{3+} + 3NO_2 + 3H_2O$

4.

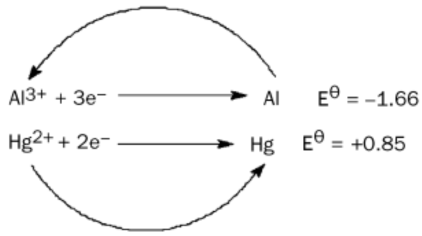
- **(i)** Aluminium.
- **(ii)** Aluminium.
- **(iii)** Mercury.
- **(iv)** Yes, tin will react with hydrochloric acid (just!): follow anticlockwise arrows.



- **(v)** Yes it can. Follow anticlockwise arrows.



(vi) No. Following anticlockwise arrows predicts that mercury stays as Hg and Al stays as Al^{3+}.



5.

(i) $Na^+(aq)$, $H^+(aq)$, $OH^-(aq)$.

(ii) Cathode: $Na^+(aq)$, $H^+(aq)$ migrate here, $H^+(aq)$ is discharged (hydrogen ions are discharged instead of sodium ions because they accept electrons more readily):

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

Anode: $OH^-(aq)$ migrate here, $OH^-(aq)$ is discharged:

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

(iii) Migration of Na^+ to the cathode and discharge of OH^- means that the concentration of NaOH(aq) falls around the anode.

6.

(i) 0.3 g: $0.2 \times 60 \times 60 = 720$ C, which corresponds to $720/96\,500 = 7.5 \times 10^{-3}$ mol electrons. Number of mol K discharged $= 7.5 \times 10^{-3}$ mol, or $7.5 \times 10^{-3} \times 39$ g.

(ii) 0.07 g.