A Level

Physical chemistry

23 Electrochemistry

In this topic, we study how a chemical reaction can produce electricity. The standard electrode potential, E^o, of an electrode system is a measure of the ease of reduction of an atom or ion. The difference between two electrode potentials gives rise to a cell potential, E ell, the size and sign of which indicates the feasibility of a reaction. In contrast, many reactions that are not otherwise feasible can be carried out by electrolysis - by passing an electric current through the reaction mixture. By choosing appropriate conditions, a wide variety of useful chemicals can be manufactured.

Learning outcomes

By the end of this topic you should be able to:

- **6.2a)** state and apply the relationship F = Le between the Faraday constant, the Avogadro constant and the charge on the electron
- **6.2b)** predict the identity of the substance liberated during electrolysis from the state of electrolyte (molten or aqueous), position in the redox series (electrode potential) and concentration
- 6.2c) calculate the quantity of charge passed during electrolysis, and the mass and/or volume of substance liberated during electrolysis, including those in the electrolysis of H2SO4(aq) and of Na2SO4(aq)
- 6.2d) describe the determination of a value of the Avogadro constant by an electrolytic method
- 6.3a) define the terms standard electrode (redox) potential and standard cell potential
- 6.3b) describe the standard hydrogen electrode
- 6.3c) describe methods used to measure the standard electrode potentials of metals or non-metals in contact with their ions in aqueous solution, and ions of the same element in different oxidation states
- 6.3d) calculate a standard cell potential by combining two standard electrode potentials
- 6.3e) use standard cell potentials to explain/deduce the direction of electron flow in a simple cell, and predict the feasibility of a reaction
- **6.3f)** deduce from E[®] values the relative reactivity of elements of Group 17 (the halogens) as oxidising agents
- 6.3g) construct redox equations using the relevant half-equations (see also Topic 24)
- 6.3h) predict qualitatively how the value of an electrode potential varies with the concentrations of the aqueous ions
- **6.3i)** use the Nernst equation, e.g. $E = E^{\Theta} + (0.059/z) \log \frac{\text{[oxidised species]}}{\text{[reduced species]}}$ to predict quantitatively how the value of an electrode potential varies with the concentrations of the aqueous ions; examples include $Cu(s) + 2e^- \rightleftharpoons Cu^{2+}(aq)$, $Fe^{3+}(aq) + e^{-} \rightleftharpoons Fe^{2+}(aq), Cl_2(g) + 2e^{-} \rightleftharpoons 2Cl^{-}(aq)$
- 6.4a) state the possible advantages of developing other types of cell, e.g. the H₂/O₂ fuel cell and the nickel-metal hydride and lithium-ion rechargeable batteries.



23.1 The electrochemical cell

Measuring electrode potentials

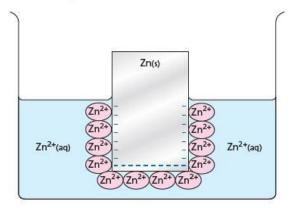
If a metal, for example zinc, is placed in a solution containing its ions, an equilibrium is set up:

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

Initially the metal begins to dissolve in the solution as metal ions, leaving the electrons on the undissolved metal. This leaves the metal negatively charged. Soon an equilibrium is established in which the rate of dissolving is balanced by ions

Figure 23.1 The equilibrium established by zinc metal in contact with its ions. A double layer of charges is formed at the surface of the

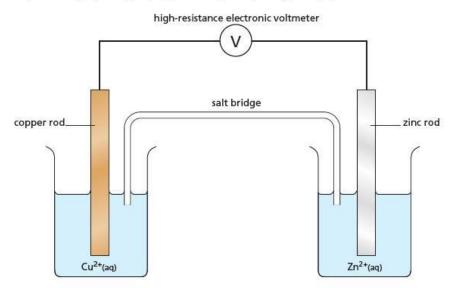
recovering electrons and re-forming the metal (see Figure 23.1). The more reactive the metal, the further to the right is the position of equilibrium and the larger is the negative charge on the metal. Therefore measuring this charge gives us a measure of the reactivity of the metal.



This charge cannot be measured by connecting one terminal of a voltmeter to the metal because a voltmeter measures **potential difference** (p.d.) and needs its other terminal to be connected to a second electrode at a different electrical potential. It would be convenient if this second electrode could be made by putting an inert metal, such as platinum, into the solution. Unfortunately this does not help, as platinum sets up its own potential which varies from experiment to experiment, depending on the solution it is immersed in, so inconsistent results are obtained. Another approach must be used.

The solution to the problem is to regard the zinc/zinc ion system as a **half-cell** and connect it to another half-cell. This will allow us to measure the potential difference between the two half-cells accurately and consistently. This means that we can only *compare* reactivities, rather than measuring them absolutely. The other half-cell could be, for example, a copper/copper ion system (see Figure 23.2).

Figure 23.2 Two half-cells are combined to make an electrochemical cell.



The voltage produced by the two half-cells depends on the conditions. As long as a high-resistance voltmeter is used, so that only a very small current is taken from the cell, and if the conditions are standard (298 K, 1.00 bar or 1.00 atm, solutions of 1.00 mol dm⁻³), the voltage is the **standard cell e.m.f.**, E_{cell}^{Θ} . (If an appreciable current is drawn from the cell, the measured voltage would be smaller than this.)

The need for a salt bridge

As mentioned above, the voltage is measured using a high-resistance electronic voltmeter. Even so, some electrons must flow and, because zinc is more reactive than copper, the following half-reactions take place to a small extent:



Figure 23.3 Copper and zinc half-cells connected together

The **standard hydrogen electrode** is the half-cell represented by the equation

 $H^{+}(aq) + e^{-} \rightleftharpoons \frac{1}{2}H_{2}(g)$, Pt under standard conditions.

Standard conditions are: p = 1.00 atm, T = 298 K and all concentrations = 1.00 mol dm⁻³.

Figure 23.4 The standard hydrogen electrode

at the zinc electrode:
$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$$
 at the copper electrode: $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$

This means that the zinc *solution* becomes positively charged, with an excess of Zn²⁺(aq) ions, and the copper *solution* becomes negatively charged, with an excess of SO₄²⁻(aq) ions, for example, if copper sulfate has been used. Because of this, the current would cease unless the circuit were completed by electrically connecting the two solutions. This cannot be done with a piece of wire, which passes only electrons, because we need to move positive *ions* one way and negative *ions* the other. (It does not matter which ions actually move, because very few of them are transferred compared with those already in the solutions.) The circuit is completed by a **salt bridge** dipping into the two solutions. Salt bridges are made from either a strip of filter paper soaked in an electrolyte (see Figure 23.3) or a bent tube packed with an electrolyte jelly, with porous plugs at the ends that allow ions to flow while minimising the mixing of the electrolytes by diffusion. The electrolyte in the salt bridge is usually potassium nitrate. This is used because all potassium compounds and all nitrates are soluble, and so no precipitate will form with any ions in contact with it.

The standard hydrogen electrode

The convention for determining the sign of the e.m.f of a cell is

$$E_{\text{cell}}^{\Theta} = E_{\text{right-hand electrode}}^{\Theta} - E_{\text{left-hand electrode}}^{\Theta}$$

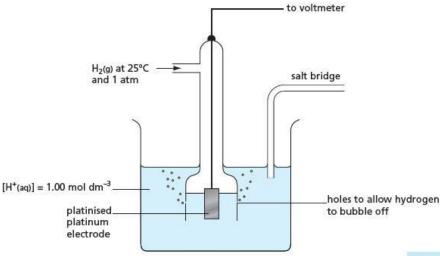
For the copper/zinc cell shown in Figure 23.2, $E_{\text{cell}}^{\bullet} = -1.075\,\text{V}$, the negative sign showing that the zinc electrode is more negative than the copper electrode. This fits in with what we know of the relative reactivities of copper and zinc: zinc ions are much less readily reduced to the metal than copper ions. This value tells us the voltage of a standard zinc half-cell compared with a standard copper half-cell. Conventionally, it has been agreed to compare all half-cells against an electrode called the **standard hydrogen electrode (SHE)**. By international agreement, this has been assigned $E^{\bullet} = 0.00\,\text{V}$. The reaction is:

$$H^+(aq) + e^- \rightleftharpoons \frac{1}{2}H_2(g)$$

This reaction is very slow to reach equilibrium, and to speed it up the hydrogen is bubbled over a platinum catalyst. The platinum surface is **platinised** – it has a spongy layer of platinum electrolysed onto it, which increases its effective surface area. The platinum is also an inert electrode, and transfers electrons to and from the circuit without taking part in any chemical reaction.

Figure 23.4 shows the standard hydrogen electrode. Its half-cell reaction is represented as:

$$H^{+}(aq) + e^{-} \rightleftharpoons \frac{1}{2}H_{2}(g)$$
, Pt



Standard electrode potential, E[⊕]

All half-cell reactions are written in the following format, with the electrons on the left:

If the voltage produced by a half-cell is measured against the standard hydrogen electrode, the cell voltage is

$$E_{\text{cell}}^{\Theta} = E_{\text{right-hand electrode}}^{\Theta} - E_{\text{left-hand electrode}}^{\Theta}$$

But since $E_{\text{left-hand electrode}}^{\Theta} = 0.00 \,\text{V}$ for the SHE,

$$E_{\text{cell}}^{\Theta} = E_{\text{right-hand electrode}}^{\Theta}$$

and the cell voltage is the **standard electrode potential**, E^{Θ} of the half-cell. The reduced form of the substance is not necessarily the free element – it may be the element in a lower oxidation state. For example, in a solution containing $1.00\,\mathrm{mol\,dm^{-3}}$ of $\mathrm{Fe^{2+}}(\mathrm{aq})$ ions and $1.00\,\mathrm{mol\,dm^{-3}}$ of $\mathrm{Fe^{3+}}(\mathrm{aq})$ ions, electrons are transferred from the $\mathrm{Fe^{2+}}(\mathrm{aq})$ ions to the $\mathrm{Fe^{3+}}(\mathrm{aq})$ ions. In order to measure the voltage for this half-cell, these electrons can be carried away on a platinum wire placed in the solution. A shiny platinum wire is used for this electrode, because it is not acting as a catalyst. The half-cell is written:

$$Fe^{3+}(aq) + e^{-} \rightleftharpoons Fe^{2+}(aq)$$
, Pt

and a diagram of it is shown in Figure 23.5.

A common error is to draw this cell with two electrodes, one dipping into $Fe^{2+}(aq)$ ions and the other dipping into $Fe^{3+}(aq)$ ions. However, both ions need to be in the same solution so that the electrode potential of the *mixture* can be measured relative to the SHE.

Many standard electrode potentials have been measured, and a few of the more important ones are listed in Table 23.1.

These standard electrode potentials are sometimes called **redox potentials**. A large negative value of E^{Θ} indicates a highly reactive metal that is easily oxidised. A large positive value of E^{Θ} indicates a highly reactive non-metal that is easily reduced. The order of these E^{Θ} values matches the observed chemical reactivity of the substances concerned, though the large negative value for lithium is surprising, since chemically it is the least reactive of the Group 1 elements.

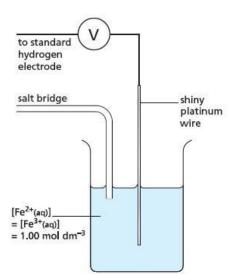


Figure 23.5 The half-cell used to measure E^{Φ} for the Fe³⁺/Fe²⁺ system. Here, [Fe³⁺] and [Fe²⁺] are shown as 1.00 mol dm⁻³. This is not essential – the important feature is that they are equal.

Cell diagrams

Instead of sketching the two half-cells, a **cell diagram** can be drawn. Cell diagrams are not really diagrams at all: they are an indication of all the chemical species involved in the whole cell make-up (including state symbols and inert electrodes, where used), written out on a single line.

Figure 23.2 (page 382) is a picture of a cell in which a zinc half-cell is compared with a copper half-cell. The cell diagram for these two half-cells is:

$$Cu(s) | Cu^{2+}(aq) | Zn^{2+}(aq) | Zn(s)$$

The solid vertical lines indicate a phase boundary, with the reduced forms on the outside, and the dotted line represents the salt bridge. (Sometimes a double dotted line is used for the salt bridge.) The concentrations of the solutions are assumed to be 1.00 mol dm⁻³ unless a different concentration is shown underneath the ions. The e.m.f. of this cell is the potential differences between the zinc rod (right-hand half-cell) and that of the copper rod (left-hand half-cell).

Table 23.1 Values of E^{Θ} for some common half-reactions. In water, in which $[H^{+}(aq)] = 10^{-7} \, \text{mol dm}^{-3}$ (that is, the conditions are non-standard), $E(H^{+}/_{2}^{1}H_{2}) = -0.41 \, \text{V}$ and $E(\frac{1}{3}O_{2}/H_{2}O) = +0.82 \, \text{V}$.

Oxidised fo	rm	Reduced fo	orm	E [⊕] /V
Weakest oxidising agents		strongest reducing agents		
	Li+(aq)		Li(s)	-3.03
	K+(aq)		K(s)	-2.92
18	Na ⁺ (aq)		Na(s)	-2.71
8	Mg ²⁺ (aq)		Mg(s)	-2.37
	Al ³⁺ (aq)		Al(s)	-1.66
	Zn ²⁺ (aq)		Zn(s)	-0.76
	Fe ²⁺ (aq)		Fe(s)	-0.44
	H ⁺ (aq)		$\frac{1}{2}H_{2}(g)$, Pt	0.00
	Cu ²⁺ (aq)		Cu(s)	+0.34
	$\frac{1}{2}I_2(aq)$		I ⁻ (aq), Pt	+0.54
	Fe ³⁺ (aq)		Fe ²⁺ (aq), Pt	+0.77
8	Ag ⁺ (aq)		Ag(s)	+0.80
	$\frac{1}{2}Br_2(aq)$		Br (aq), Pt	+1.09
	$\frac{1}{2}O_2(g)$, Pt + 2H ⁺ (aq)		H ₂ O(I)	+1.23
	1/2 Cl₂(aq)		Cl-(aq), Pt	+1.36
	MnO ₄ ⁻ (aq) + 8H ⁺ (aq)		Mn ²⁺ (aq), Pt	+1.51
strongest oxidising agents	$\frac{1}{2}$ F ₂ (aq)	weakest reducing agents	F-(aq), Pt	+2.87

Worked example

Write a cell diagram for:

- a magnesium electrode compared with the standard hydrogen electrode
- b a Fe³⁺(aq)/Fe²⁺(aq) half-cell compared with a zinc half-cell.

Answer

a Pt, ¹/₂H₂(g) |H⁺(aq) |Mg²⁺(aq) | Mg(s)

(Note: some textbooks use 'Pt $[\frac{1}{2}H_2(g)]$ ' rather than 'Pt, $\frac{1}{2}H_2(g)$ '.)

b Zn(s) | Zn²⁺(aq) | Fe³⁺(aq), Fe²⁺(aq) | Pt

Here, Fe³⁺(aq) and Fe²⁺(aq) are separated by a comma because they are in the same phase.

Calculating the standard e.m.f. of a cell, E cell

The values of E^{Θ} shown in Table 23.1 can be used to work out the standard e.m.f. of a cell, E^{Θ}_{cell} . Conventionally this is the voltage of the right-hand half-cell measured against the left-hand half-cell. So:

The standard e.m.f. of a cell

 $E_{\text{cell}}^{\oplus} = E_{\text{right-hand half-cell}}^{\oplus} - E_{\text{left-hand half-cell}}^{\oplus}$

Now try this

Write cell diagrams for:

- 1 a Cr³⁺(aq)/Cr²⁺(aq) half-cell compared with a copper half-cell
- 2 an Al³⁺(aq)/Al(s) half-cell compared with a chlorine half-cell
- 3 a [MnO₄⁻(aq) + 8H⁺(aq)]/Mn²⁺(aq) halfcell compared with a bromine half-cell (include H⁺(aq) ions and H₂O(l))
- 4 an [O₂(g) + 2H⁺(aq] half-cell compared with the SHE half-cell.

Worked example

- a Calculate E^o_{cell} for a copper electrode compared with a zinc electrode.
- b Calculate E[⊕]_{cell} for the following cell: Pt | Fe²⁺(aq), Fe³⁺(aq) | Ag⁺(aq) | Ag(s)

Answer

- a E_{cell}^{Θ} = +0.34 (-0.76) = +1.10 V (It is a good idea always to include the sign.)
- **b** $E_{cell}^{\Theta} = +0.80 (+0.77) = +0.03 \text{ V}$

Now try this

Draw the experimental set-up, write the cell diagram and calculate E_{cell}^{\oplus} for each of the following cells.

- 1 a magnesium electrode compared with a zinc electrode
- 2 a chlorine electrode compared with a bromine electrode
- 3 an oxygen electrode compared with a copper electrode

23.2 Using E_{cell}° values to measure the feasibility of reactions

When the two electrodes of a cell are connected to each other, electrons flow from the negative electrode to the positive electrode. Chemical changes take place at each electrode that reduce the voltage produced by the cell (the terminal p.d.), and finally the reaction stops because the two electrodes are at the same electrical potential. If E_{cell}^{Θ} is positive, the reaction corresponding to the cell diagram takes place from left to right. For example, the cell diagram:

$$Zn(s) | Zn^{2+}(aq) | Cu^{2+}(aq) | Cu(s)$$
 $E_{cell}^{\bullet} = +1.10 V$

corresponds to the reaction:

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

and, as E_{cell}^{Θ} is positive, the reaction is feasible and should take place if zinc is added to copper sulfate solution. In this case, experiment confirms that the prediction is correct. In other cases, this does not happen. There are two reasons why this may be so, and we shall look at each in turn.

Non-standard conditions

When determining $E_{\rm cell}^{\bullet}$, all solutions have a concentration of 1.00 mol dm⁻³. This is unlikely to be the case if the reaction is carried out in a test tube. For the zinc/copper sulfate reaction, the voltage is so large and positive that changing the concentrations has no effect. However, the situation is different if $E_{\rm cell}^{\bullet}$ is less than +0.2 V – under these conditions, a fairly small change in concentration could make the voltage become negative and the reaction is then not feasible. Non-standard conditions are discussed further in section 23.3.

High activation energy

Many reactions, particularly those involving gases and solutions, have a high activation energy. Although the $E_{\rm cell}^{\Theta}$ value may indicate that the reaction is feasible, it is often so slow that no change is observed if it is carried out in the test tube. For example, $E_{\rm cell}^{\Theta}$ for Cu²⁺/Cu is +0.34V. This suggests that hydrogen gas should react with copper sulfate solution, but no reaction is observed when hydrogen is bubbled through a solution of copper sulfate. The slowness of the conversion of gases into ions is the reason why platinised platinum is used in the standard hydrogen electrode.

Just as the conversion of $H_2(g)$ to $H^+(aq)$ ions has a high activation energy, so too does the reverse process. This means that the production of hydrogen (and oxygen as well) by electrolysis often requires a greater voltage than is predicted by the E_{cell}^{Θ} values. This means that hydrogen and oxygen often need an **overvoltage** before they are discharged.

Worked example

Use E^{Θ} values from Table 23.1 to calculate E^{Θ}_{cell} for the following reactions, and hence predict whether they are feasible:

a
$$Zn(s) + Mg^{2+}(aq) \rightarrow Zn^{2+}(aq) + Mg(s)$$

b
$$Cl_2(aq) + H_2O(1) \rightarrow \frac{1}{2}O_2(g) + 2CF(aq) + 2H^+(aq)$$

Answer

a $E_{\text{cell}}^{\bullet} = E^{\bullet}(\text{Mg}^{2+}/\text{Mg}) - E^{\bullet}(\text{Zn}^{2+}/\text{Zn}) = -2.37 - (-0.76) = -1.61 \text{V}$ The reaction is not feasible.

b
$$E_{\text{cell}}^{\Theta} = E_{\text{cell}}^{\Theta} = \frac{1}{2} \text{Cl}_2/\text{C} + 0 - E_{\text{cell}}^{\Theta} = \frac{1}{2} \text{O}_2/\text{H}_2 = +1.36 - (+1.23) = +0.13 \text{ V}$$

The reaction is feasible. Cl⁻ and H₂O are the reduced forms.

Now try this

1 Use E^{Θ} values from Table 23.1 to calculate E^{Θ}_{cell} and hence predict whether the following reactions are feasible.

(Hint: you may find section 7.1 helpful in writing the relevant half-equations.)

$$\frac{1}{2}H_2(g) + Ag^+(aq) \to H^+(aq) + Ag(s)$$

b MnO₄⁻(aq) + 5CF(aq) + 8H⁺(aq) → Mn²⁺(aq) + 4H₂O(I) +
$$2\frac{1}{2}$$
Cl₂(aq)

- c Fe(s) + 2Fe³⁺(aq) \rightarrow 3Fe²⁺(aq)
- d Ag+(aq) + Fe²⁺(aq) \rightarrow Fe³⁺(aq) + Ag(s)
- 2 Iodide reacts slowly with aqueous peroxydisulfate(VI) ions to produce iodine and sulfate ions:

$$2I^{-}(aq) + 2S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

It has been found that the best catalysts for this reaction are transition metal cation-pairs whose E^{Θ} values lie between those of I_2/I^- (+0.54 V) and $S_2O_8^{2-}/SO_4^{2-}$ (+2.01 V). Thus Fe^{3+}/Fe^{2+} ($E^{\Theta}=+0.77$ V), Ce^{4+}/Ce^{3+} ($E^{\Theta}=+1.70$ V) and Co^{3+}/Co^{2+} ($E^{\Theta}=+1.81$ V) are all effective. Anion-pairs such as CIO^-/CI^- ($E^{\Theta}=+0.89$ V) are not effective, however.

- Suggest why the reaction can be catalysed by cations, but not by anions.
- b Use the E[®] data given above to calculate E[®] for each of the two redox reactions, and hence show that each reaction is feasible.



Figure 23.6 An untreated iron gate rusts when exposed to air and water.

Corrosion

All reactive metals **corrode** – they react with oxygen and water in the air. Some, for example aluminium and chromium, form a thin layer of oxide that protects them from further attack. Iron readily **rusts** to form hydrated iron(III) oxide, Fe₂O₃.H₂O or FeO.OH. Unlike the oxides of aluminium and chromium, this does not stick well to the metal surface. It easily flakes off and exposes more of the surface to further corrosion.

Rusting is a complex electrochemical process that takes place most readily under the following conditions:

- . some of the iron is in contact with air while other regions are not
- the iron is in contact with water containing salt or other ionic substances.

In contact with air, the following reaction takes place:

$$1\frac{1}{2}O_2 + 3H_2O + 6e^- \rightarrow 6OH^ E^{\Theta} = +0.81 \text{ V at pH } 7$$

In the air-free region, iron dissolves:

$$2\text{Fe} \rightarrow 2\text{Fe}^{3+} + 6\text{e}^{-}$$
 $E^{\Theta} = -0.04\text{ V}$

The overall equations are:

$$2\text{Fe(s)} + 1\frac{1}{2}\text{O}_2(\text{g}) + 3\text{H}_2\text{O(l)} \rightarrow 2\text{Fe}^{3+} + 6\text{OH}^-$$

 $2\text{Fe}^{3+} + 6\text{OH}^- \rightarrow 2\text{FeO.OH(s)} + 2\text{H}_2\text{O}$

The electrons flow in the metal from the air-rich to the air-free region. This takes place more quickly if the resistance of the solution that completes the circuit is lowered by the addition of salt.

Corrosion can be minimised in several ways. These include:

- · painting or covering the iron in plastic to exclude air
- · coating iron with another metal, for example zinc, tin or chromium
- · alloying the iron, for example with chromium
- fixing a more reactive metal, such as magnesium, to the iron. The reactive metal
 preferentially dissolves and the process is therefore called sacrificial protection
 or anodic protection. Magnesium dissolves, having a more negative E[®] value
 (-2.37V) than iron, keeping the iron negative and discouraging the reaction:

$$Fe \rightarrow Fe^{3+} + 3e^{-}$$



Figure 23.7 Walther Nernst

23.3 The Nernst equation

Non-standard conditions

In Figure 23.2, we showed a zinc half-cell connected to a copper half-cell. Under standard conditions, $E_{\rm cell}^{\Theta} = +1.10 \, {\rm V}$ and, when the cell passes current, electrons flow from the zinc to the copper rod. If we now reduce the concentration of the zinc ions in the zinc half-cell, the equilibrium

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

is displaced to the left and the negative charge on the zinc rod becomes bigger. Qualitatively this can be predicted from Le Chatelier's Principle (see section 9.2), and it always happens when the concentration of the oxidised form is reduced below the standard value of 1.0 mol dm⁻³.

This change in the value of E_{cell}^{Θ} from non-standard conditions can be calculated using the Nernst equation, named after Walther Nernst (Figure 23.7).

For a half-cell against a standard hydrogen electrode at room temperature, this equation can be written as:

$$E = E^{\Theta} + (0.059/z) \log \frac{\text{[oxidised species]}}{\text{[reduced species]}}$$

where z is the number of electrons added to the oxidised species to form the reduced species.

A ten-fold change in concentration only affects the E^{Θ} value by 0.059 V for a single electron transfer and 0.030 V for the transfer of two electrons. These are very small changes and this is the reason why E^{Θ} values are such a good guide to the feasibility of the reaction, even under non-standard conditions.

Worked example 1

What is E for a copper electrode dipping into a solution of 0.000 10 mol dm⁻³ Cu²⁺(aq) ions? $[Cu^{2+} + 2e^- \rightleftharpoons Cu \quad E^{\bullet} = +0.34 \text{ V}]$

Answer

$$E = E^{\Theta} + (0.059/z) \log \frac{\text{[oxidised species]}}{\text{[reduced species]}}$$

The reduced species is metallic copper which is also the reduced species in the standard electrode potential. This means that the value of [reduced species] has been incorporated into E^{Θ} and can be ignored.

E = +0.34 +
$$\frac{0.059}{2}$$
 log 1.0 × 10⁻⁴
= +0.34 + $\frac{(0.059 \times -4)}{2}$
= +0.34 - 0.118 = +0.22

However if the concentration changes are very large, the change in E_{cell}^{Θ} becomes significant. We will look at the following three examples:

- for a sparingly soluble salt
- for changes in pH
- for the formation of complex ions. (This will be considered in section 24.4.)

Sparingly soluble salt

Worked example 2

A silver electrode dips into a saturated solution of silver bromide which has a solubility of 7.1×10^{-7} mol dm⁻³. What is *E* for this half-cell?

$$[Ag^+ + e^- \rightleftharpoons Ag \quad E^{\Theta} = 0.80 \text{ V}]$$

Answer

$$E = E^{\oplus} + (0.059/z) \log \frac{\text{[oxidised species]}}{\text{[reduced species]}}$$

The value of [reduced species] is incorporated in E^{Θ} and is ignored.

[Ag⁺] =
$$7.1 \times 10^{-7} \text{ mol dm}^{-3}$$

 $E = 0.80 + \frac{0.059}{1} \times (-6.15)$

Changes in pH

A typical pH meter consists of a glass electrode (which allows the passage of H⁺ ions) attached to a reference electrode by a salt bridge. Frequently the H⁺ concentration varies between $1.0 \, \text{mol dm}^{-3}$ (e.g. $1.0 \, \text{mol dm}^{-3}$ HCl) and $10^{-14} \, \text{mol dm}^{-3}$ (e.g. $1.0 \, \text{mol dm}^{-3}$ NaOH). This has a profound effect on the E_{cell} values and forms the basis

Now try this

- 1 $K_{\rm sp}$ for AgCl is $2.0 \times 10^{-10} \, {\rm mol^2 dm^{-6}}$. What is E for a silver electrode when it is placed in
- a a saturated solution of silver chloride
- b in a solution of silver chloride in 0.10 mol dm⁻³ KCl?
- 2 (Harder) Brine is saturated sodium chloride solution, whose concentration is 0.50 mol dm⁻³. When this solution is electrolysed, chlorine gas is formed until a saturated solution is formed. Because chlorine reacts with water, the concentration of free chlorine in a saturated solution is only 0.030 mol dm⁻³. Calculate E for the reaction Cl₂(aq) +2e⁻ ⇌ 2Cl⁻(aq) under these conditions.

for the accurate measurement of pH. Because $pH = -log[H^+]$, we can write the Nernst equation in the form

$$E_{\text{cell}} = E_{\text{cell}}^{\Theta} - 0.059 \times \text{pH}$$

Now try this

Using the same electrode system as in the example above, what is the $E_{\rm cell}$ value when the glass electrode dips into a solution of

1 0.05 moldm⁻³ NaOH

2 0.10 mol dm⁻³ ethanoic acid $(K_a = 1.8 \times 10^{-5} \text{ mol dm}^{-3})$?

Worked example 3

The reference electrode in a pH meter is a silver/silver chloride electrode with

$$E_{cell}^{\Theta} = +0.23 \text{ V}$$

What is the E_{cell} value when it and a glass electrode dip into a solution of pH3?

Answei

$$E_{\text{cell}} = E_{\text{cell}}^{\bullet} - 0.059 \times \text{pH}$$

 $E_{\text{cell}} = +0.23 - 3 \times 0.059$
 $= +0.053 \text{V}$

Figure 23.8 Michael Faraday (1791–1867). One of his many achievements was to establish a quantitative basis for electrochemistry.

23.4 The Faraday constant

When current flows from the copper/zinc cell, the following changes take place:

at the negative electrode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ at the positive electrode: $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$

During electrolysis, however, current is forced through the cell in the other direction and the reverse processes take place:

at the cathode: $Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$ at the anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$

In order to deposit one mole of zinc and dissolve one mole of copper, two moles of electrons need to be passed through the cell. One mole of electrons carries a charge of $-96500\,\mathrm{C}$. This is the same charge as the charge on one electron, $1.603\times10^{-19}\,\mathrm{C}$, multiplied by the Avogadro constant, $6.022\times10^{23}\,\mathrm{mol}^{-1}$. Numerically, the same amount of charge is carried by one mole of protons; this quantity is called the **Faraday constant**, F, and has a value of $96500\,\mathrm{C\,mol}^{-1}$.

The **coulomb** (symbol C) is the unit of electrical charge. One coulomb is the amount of charge that is passed when one ampere flows for one second. Hence the amount of charge passed in time t is:

$$I \times t$$

The amount of charge on one mole of z+ ions is zF, and so the number of moles deposited is given by:

$$amount = \frac{charge passed}{charge per mole of ions} = \frac{I \times t}{zF} mol$$

where z is the charge on the ion, I the current in amperes and t the time in seconds.

The amount liberated may be converted to a mass by multiplying by the molar mass. Alternatively, if the products are gaseous, the amount may be multiplied by $24\,\mathrm{dm}^3$ to obtain the volume of gas produced at room temperature and pressure.

Electrolysis may also be used to find the value of the Avogadro constant. The value of the Faraday constant is first determined from an electrolysis experiment, for example by depositing copper from a solution containing $Cu^{2+}(aq)$ ions. A steady current, I, is passed for a measured time, t (in seconds), and the mass, m, of copper deposited is measured. We have:

$$\frac{m}{63.5} = \frac{I \times t}{2F}$$

The electrolysis experiment gives a value for the Faraday constant of $96500 \,\mathrm{C}\,\mathrm{mol}^{-1}$, that is, $96500 \,\mathrm{C}$ is one mole of electrons. Experiments in physics have shown that the charge on each electron is $1.60 \times 10^{-19} \,\mathrm{C}$.

Now try this

- 1 Calculate the mass of aluminium produced when a current of 1000 A is passed through a cell containing Al³⁺ ions for 1 hour.
- 2 a Show that 0.0016 mol of oxygen is produced when a current of 1.0 A is passed through sulfuric acid solution for 10 minutes.
 - b Calculate the volume of oxygen that should be liberated.
 - Suggest why the actual volume collected may be less than this.
- 3 Explain why:
 - hydrogen and oxygen are evolved when aqueous sodium hydroxide is electrolysed
 - b when aqueous copper sulfate is electrolysed with platinum electrodes, the cathode becomes plated with copper and oxygen is evolved at the anode
 - when aqueous copper sulfate is electrolysed with copper electrodes, the anode dissolves.

Figure 23.9 Voltage–current graph for a copper/zinc cell. At 1.10 V, no current flows. Above 1.10 V, electrolysis takes place. The reaction runs in reverse and it is Zn²⁺(aq) that is reduced.

Thus:

$$L \times 1.603 \times 10^{-19} = 96500$$

$$L = \frac{96500}{1.603 \times 10^{-19}}$$

$$= 6.03 \times 10^{23} \text{ mol}^{-1}$$

Worked example

Calculate the mass of copper that dissolves when a current of 0.75A is passed through a zinc/copper cell for 45 minutes. $[A_r(Cu) = 63.5]$

Answe

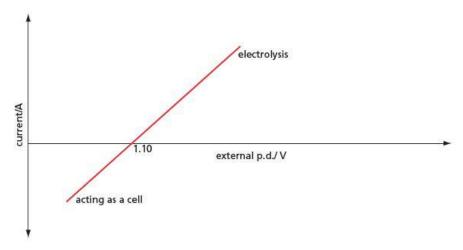
amount =
$$\frac{l \times t}{zF} = \frac{0.75 \times 45 \times 60}{2 \times 96500} = 0.0105 \text{mol}$$

mass of copper = $0.0105 \times 63.5 = 0.67 \text{ g}$

23.5 Electrolysis

Pushing the cell reaction in the opposite direction

If the electrodes of a cell are connected together, electrons flow from the negative to the positive terminal. If, instead, the terminals are connected to an external voltage supply and the applied voltage is gradually increased, electrons still flow as before until the external voltage equals $E_{\rm cell}$. At this voltage no current flows. If the external voltage is increased still further, current flows in the opposite direction and **electrolysis** takes place (see Figure 23.9).



During electrolysis, positively charged ions, called **cations**, gain electrons at the negatively charged electrode (the **cathode**). At the same time negatively charged ions, called **anions**, give up electrons at the positively charged electrode (the **anode**).

 $E_{\rm cell}$ therefore is the minimum voltage required to bring about electrolysis. In practice, the voltage used for electrolysis is always greater than this minimum. There are two reasons for this.

- The cell has resistance, so an additional voltage is needed to drive current through the cell.
- The cell discharge often requires an 'overvoltage' to overcome a high activation energy associated with the discharge. This is particularly important when hydrogen or oxygen is being produced by electrolysis of aqueous solutions.

Molten salts

When solid, a salt will not conduct electricity because the ions are not free to move. When molten, however, the ions can move and the salt starts to conduct electricity. The conductivity often increases as the temperature is raised because there is less viscous drag on the ions to limit how fast they can move.

The electrolysis of molten salts is used to produce reactive elements, such as the alkali metals, that cannot be formed by electrolysing aqueous solutions, because they react with water. For example:

Selective discharge

In an electrolysis cell, the electrolyte may contain several cations or anions. Under these circumstances, the one that is discharged is the one that requires the least energy. This is called **selective discharge**. For example, if a mixture of copper chloride and zinc chloride is electrolysed, copper rather than zinc is deposited at the cathode. This is because E^{Θ} for the Cu²⁺/Cu half-cell is closer in value to E^{Θ} for the Cl₂/Cl⁻ half-cell than E^{Θ} for the Zn²⁺/Zn half-cell is. This shows that copper requires a smaller potential difference to be discharged than zinc does (see Table 23.2).

Table 23.2 In a solution containing copper chloride and zinc chloride, copper rather than zinc is deposited at the cathode because a smaller voltage is needed to bring about the electrolysis.

Cation	Anion	E [⊕] _{cell}	
$E^{\Theta}(Zn^{2+}/Zn) = -0.76 \text{ V}$	$E^{\Theta}(\frac{1}{2}Cl_2/Cl^2) = +1.36V$	2.12V	
$E^{\Theta}(Cu^{2+}/Cu) = +0.34V$	$E^{\Theta}(\frac{1}{2}Cb/CF) = +1.36V$	1.02 V	

In aqueous solutions, $H_3O^+(aq)$ and $OH^-(aq)$ ions are present and so selective discharge takes place. If dilute sulfuric acid is electrolysed, for example, hydrogen is liberated at the cathode because the only cation present is the $H_3O^+(aq)$ ion. There are, however, both $OH^-(aq)$ ions and $SO_4^{\ 2}(aq)$ ions in solution. A study of $E^{\ \Theta}$ values (see Table 23.3) predicts that oxygen should be liberated at the anode:

$$2OH^{-}(aq) \rightarrow H_2O(1) + O_2(g) + 2e^{-}$$

Cathode	Anode	E cell
$E^{\Theta}(H^{+}/\frac{1}{2}H_{2}) = 0.0V$	$\frac{1}{2}O_2/OH^- = +1.23 \text{ V}$ $[OH^-] = 10^{-14} \text{mol dm}^{-3}$	1.23V
$E^{\Theta}(H^{+}/\frac{1}{2}H_{2}) = 0.0 \text{ V}$	$\frac{1}{2}S_2O_8^2 - /SO_4^2 - = 2.01 \text{ V}$	2.01 V

Because both hydrogen and oxygen have a high overvoltage, they are often not discharged even though E^{Θ} values suggest that they should be. For example, the electrolysis of brine usually yields chlorine rather than oxygen and it is possible in aqueous solution to electroplate objects with metals (for example, nickel) that have negative values of E^{Θ} for their half-cells.

Table 23.3 The E_{cell}^{Θ} values predict that hydrogen and oxygen are evolved in the electrolysis of dilute sulfuric acid.

23.6 Other types of cells

Fuel cells

When the gases heated by burning a fossil fuel are used to drive a piston or to turn the blades of a turbine, the overall efficiency is always low, no matter how well the plant is designed. The typical efficiency of a motor car is 20%, and that of a power station is 40%. This is a thermodynamic limitation: the only way to raise the efficiency is to use a higher operating temperature. This in turn produces fresh problems.

In order to achieve higher efficiencies, efforts have been made to convert the fuel directly into electrical energy by means of a **fuel cell**. The obvious pollution-free fuel is hydrogen, which can be burnt in air to produce water. The reactions are the reverse of the electrolysis of water. In acidic solution, we have:

at the negative plate: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$

at the positive plate: $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O(1)$

In alkaline conditions:

at the negative plate: $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$

at the positive plate: $\frac{1}{2}O_2 + H_2O(1) + 2e^- \rightarrow 2OH^-(aq)$

The problem is that the reactions at the electrodes are slow, even when the electrodes are made of platinum, which acts as a catalyst. There is a further complication for cars in that the hydrogen must be transported, either in heavy cylinders or at very low temperatures as a liquid. Efforts are being made to carry the hydrogen in the form of transition metal hydrides, but these are costly and can absorb only a limited amount of hydrogen.

As an alternative to transporting hydrogen to fuel cars, methanol is a fuel that is easy to carry and can be broken down to produce carbon dioxide and hydrogen. This introduces an additional stage in the process, and there is also the danger that some poisonous carbon monoxide may be produced in addition to the carbon dioxide. Attempts are therefore being made to produce fuel cells that use methanol directly, but these cells are only partially successful as they have to be operated above room temperature.

In the final analysis, fuel cells are really only another form of storage battery. In the first place, the hydrogen must have been produced chemically, possibly by electrolysis, and this process is not pollution-free. At present, a promising line of development is to use a hybrid system, running the car on electricity in towns where pollution is the main problem, and then, on the open road, using a traditional fuel to recharge the batteries.

Rechargeable batteries

Theoretically, most cells can be recharged when they run down, but in practice there are difficulties if the recharging is carried out quickly. The problem may be that metals are not re-deposited in an even layer, or that gaseous hydrogen and oxygen are given off.

The familiar lead-acid accumulator (the traditional 'car battery') has lead plates dipping into moderately concentrated sulfuric acid. After the first charging, the positive plate becomes covered with a layer of lead(IV) oxide. During discharge, the following reactions take place:

at the negative plate: $Pb(s) + H_2SO_4(aq) \rightarrow PbSO_4(s) + 2H^+(aq) + 2e^-$

at the positive plate: $PbO_2(s) + H_2SO_4(aq) + 2H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(1)$

During recharging, the reactions are reversed. Because sulfuric acid is a good conductor of electricity, the internal resistance of the lead–acid cell is very low. This means that it can produce very large currents, making it suitable for powering the starter motor in a car. Its disadvantage is its low power-to-weight ratio and the fact that the battery must be kept upright.

Because lead—acid cells are so heavy, other rechargeable cells have been developed which are more expensive but which give a better power-to-weight ratio. A common one is the nickel-hydride or NiMH cell. NiMH cells have largely taken over from the older nickel-cadmium cells because they have about three times the storage capacity. Like the nickel-cadmium cell, the positive electrode is nickel hydroxide and the electrolyte is potassium hydroxide. The main difference is that instead of cadmium



Figure 23.10 Rechargeable batteries. The chemical reactions that take place at each electrode must be reversible. Side reactions limit the number of recharging cycles that can be achieved – for most cells this is about 1000.

(which is highly toxic), the negative electrode is a metal M that can absorb hydrogen to make a hydride. When charging, the following changes take place:

at the positive electrode: $Ni(OH)_2 + OH^- \rightarrow NiO(OH) + H_2O + e^-$

at the negative electrode: $H_2O + M + e^- \rightarrow OH^- + MH$

The metal M is either a mixture of rare earth metals or a mixture of transition metals. A big advantage of NiMH cells is that when they are fully charged any oxygen given off combines with the metal hydride to form water. A cell can, therefore, be sealed and used in any position. A disadvantage is that the charge leaks away and after a fortnight a cell will have lost about half of its charge.

Other modern rechargeable cells are based on lithium. They have the following advantages over the lead-acid cell: they are light, they produce a large voltage and they can be used in a sealed container. Their disadvantages are that they are expensive and must be treated carefully as they contain very reactive chemicals. In these cells, lithium ions move from the positive to the negative electrode (not electrons as in the lead-acid cell). The negative electrode is a mixed lithium-transition metal oxide such as LiCoO₂. The positive electrode is graphite and the electrolyte is a lithium salt dissolved in an organic solvent.

When charging, the following reactions take place:

at the positive electrode: LiCoO₂ → CoO₂ + Li⁺ + e⁻

at the negative electrode: Li+ + e- + graphite → Li(graphite)

At the positive electrode, some of the cobalt changes from Co(III) to Co(IV), releasing electrons (which go to the positive terminal of the charger) and lithium ions (which migrate through the electrolyte to the negative electrode). At the negative electrode, lithium ions are attracted by the free electrons in the layers of graphite and form lithium atoms sandwiched between the layers of graphite. The electrons are supplied by the negative terminal of the charger.

During discharge, the reverse of the charging reactions takes place. At the negative electrode each lithium atom gives up its outer electron to form lithium ions. These electrons flow through external circuit, giving up their energy. At the same time, lithium ions move through the electrolyte and combine with CoO_2 to give $LiCoO_2$. This process requires the addition of the electrons which have moved through the external circuit. Other transition metals, such as iron, manganese and nickel, are also used instead of cobalt in the positive electrode.

In a discussion about the merits of each type of rechargeable cell, the following are some of the factors that need to be considered.

- · Cost: lead-acid is the cheapest.
- Power-to-weight ratio: lithium is the best.
- Safety: NiMH can be used in any position and the chemicals they contain are relatively safe.

Summary

A metal dipping into a solution of its ions forms a half-cell.
 When this is connected to another half-cell by means of salt bridge, an electrochemical cell is set up. Under standard conditions, the voltage set up by this cell is the standard cell e.m.f., E[®]_{cell}, for the cell.

$$E_{\text{cell}}^{\Theta} = E_{\text{right-hand half-cell}}^{\Theta} - E_{\text{left-hand half-cell}}^{\Theta}$$

- If the left-hand half-cell is the standard hydrogen electrode, the standard cell e.m.f. is the standard electrode potential, E^e, for the right-hand half-cell.
- The value of E[®] measures the oxidising/reducing power of the half-cell system, and the feasibility of redox reactions can be predicted from E[®]_{cell} values.
- A redox reaction that is predicted to be feasible from E^Φ_{cell} values might not take place in practice, either because the conditions are non-standard or because the activation energy is very high.
- If the conditions are non-standard, the **Nernst equation** in the form $E = E1 + (0.059/z) \log \frac{[\text{oxidised species}]}{[\text{reduced species}]}$ can be used to calculate the cell voltage.

- Electrolysis is the process of driving a reaction that is not thermodynamically feasible by passing an electric current through it.
- The ions that are discharged in electrolysis are the ones that require the least energy.
- The amount of substance in moles dissolved or deposited during electrolysis is given by:

$$amount = I \times \frac{t}{zF}$$

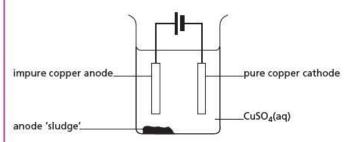
where I is the current, t the time in seconds, z the charge on the ion and F the Faraday constant.

• If e is the charge on an electron, then Le = F.

Examination practice questions

Please see the data section of the CD for any $A_{\rm r}$ values you may need.

1 The electrolytic purification of copper can be carried out in an apparatus similar to the one shown below.



The impure copper anode contains small quantities of metallic nickel, zinc and silver, together with inert oxides and carbon resulting from the initial reduction of the copper ore with coke. The copper goes into solution at the anode, but the silver remains as the metal and falls to the bottom as part of the anode 'sludge'. The zinc also dissolves.

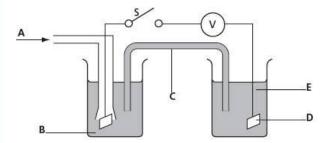
- a i Write a half-equation including state symbols for the reaction of copper at the anode.
 - ii Use data from the data section on the CD to explain why silver remains as the metal.
 - iii Use data from the data section on the CD to predict what happens to the nickel at the anode.
 - iv Write a half-equation including state symbols for the main reaction at the cathode.
 - v Use data from the data section on the CD to explain why zinc is not deposited on the cathode.

- vi Suggest why the blue colour of the electrolyte slowly fades as the electrolysis proceeds. [7]
- b Most of the current passed through the cell is used to dissolve the copper at the anode and precipitate pure copper onto the cathode. However, a small proportion of it is 'wasted' in dissolving the impurities at the anode which then remain in solution. When a current of 20.0 A was passed through the cell for 10.0 hours, it was found that 225 g of pure copper was deposited on the cathode.
 - i Calculate the following, using appropriate data from the data section on the CD.
 - number of moles of copper produced at the cathode
 - number of moles of electrons needed to produce this copper
 - number of moles of electrons that passed through the cell
 - ii Hence calculate the percentage of the current through the cell that has been 'wasted' in dissolving the impurities at the anode. [4]
- c Nickel often occurs in ores along with iron. After the initial reduction of the ore with coke, a nickel-iron alloy is formed. Use data from the data section on the CD to explain why nickel can be purified by a similar electrolysis technique to that used for copper, using an impure nickel anode, a pure nickel cathode, and nickel sulfate as the electrolyte. Explain what would happen to the iron during this process.

[Cambridge International AS & A Level Chemistry 9701, Paper 41 Q3 November 2010] 2 Chlorine gas and iron(II) ions react together in aqueous solution as follows.

$$Cb + 2Fe^{2+} \rightarrow 2C\Gamma + 2Fe^{3+}$$

a The following diagram shows the apparatus needed to measure the E_{cell}^{Θ} for the above reaction.



- Identify what the five letters A E in the above diagram represent.
- ii Use the data section on the CD to calculate the E^e_{cell} for this reaction, and hence decide which direction (left to right, or right to left) electrons would flow through the voltmeter V when switch S is closed. [7]
- b Iron(III) chloride readily dissolves in water.

$$FeCl_3(s) \rightarrow Fe^{3+}(aq) + 3C\Gamma(aq)$$

 Use the following data to calculate the standard enthalpy change for this process.

Species	∆H ^o _f /kJ mol ⁻¹	
FeCl ₃ (s)	-399.5	
Fe ³⁺ (aq)	-48.5	
Ch(aq)	-167.2	

ii A solution of iron(III) chloride is used to dissolve unwanted copper from printed circuit boards. When a copper-coated printed circuit board is immersed in FeCl₃(aq), the solution turns pale blue.

Suggest an equation for the reaction between copper and iron(III) chloride and use the data section on the CD to calculate the E^o for the reaction. [4] [Cambridge International AS & A Level Chemistry 9701, Paper 4 Q1 June 2008]

- 3 a State the relationship between the Faraday constant, *F*, the charge on the electron, *e*, and the Avogadro number, *L*.
 - b If the charge on the electron, the A_r and the valency of copper are known, the value of the Avogadro number can be determined experimentally. This is done by passing a known current for a known time through a copper electrolysis cell, and weighing the mass of copper deposited onto the cathode.

[1]

 Draw a diagram of suitable apparatus for carrying out this experiment. Label the following: power supply (with + and – terminals); anode; cathode; and ammeter.

State the composition of the electrolyte. The following are the results obtained from one such experiment.

current passed through the cell = 0.500 A time current was passed through cell = 30.0 min initial mass of copper cathode = 52.243 g final mass of copper cathode = 52.542 g

- ii Use these data and relevant information from the data section on the CD to calculate a value of L to
 3 significant figures. [9]
- c Use relevant information from the data section on the CD to identify the substances formed at the anode and at the cathode when aqueous solutions of the following compounds are electrolysed.
 [5]

Compound	Product at anode	Product at cathode
AgF		
FeSO ₄		
MgBr ₂		

[Cambridge International AS & A Level Chemistry 9701, Paper 42 Q3 June 2011]