Cambridge A2 level Chemistry

CODE: (9701)

Chapter 20

Electrochemistry

Redox reactions revisited

You learned to create redox reaction equations using relevant half-equations and utilized oxidation numbers to indicate oxidation or reduction of a reactant in a chemical reaction.
■The species (atom, ion or molecule) losing electrons is being oxidized. It acts as a reducing agent.
■The species gaining electrons is being reduced. It acts as an oxidizing agent.

Electrolysis

Electrolytic cells

Electrolysis is the process of breaking down a compound into its elements using an electric current, often used to extract high-reactivity metals, produce non-metals like chlorine, and purify some metals.

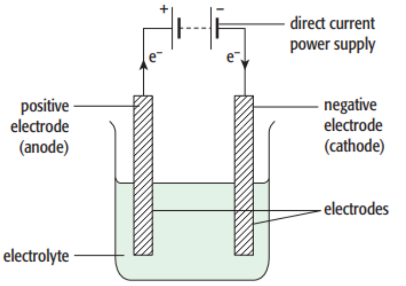


Figure 20.2 The main parts of an electrolysis cell. The actual structure of the cell will vary according to the element extracted. The e⁻ shows the direction of travel of the electrons around the external circuit.

In the electrolysis cell:
■The **electrolyte** is the compound that is decomposed; it is either molten ionic compound or a concentrated aqueous solution of ions
■The **electrodes** are rods, made from either carbon (graphite) or metal, which conducts electricity to and from the electrolyte
– the **anode** is the positive electrode
– the **cathode** is the negative electrode
■The power supply must be direct current

Redox reactions in electrolysis

During electrolysis, the positive ions (cations) move to the cathode. When they reach the cathode, they gain electrons from the cathode. For example:
Cu^{2+} + 2e -------- Cu
2H+ + 2e----------- H_2

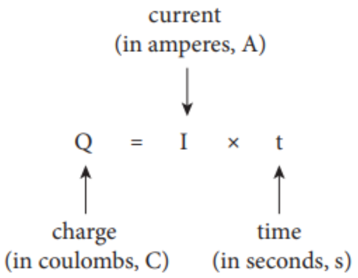
The negative ions (anions) move to the anode. When they reach the anode, they lose electrons to the anode. For example:
$2Cl \rightarrow Cl_2 + 2e^-$
$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

Loss of electrons is oxidation. Oxidation always occurs at the anode. Electrolysis is a redox reaction.

Quantitative electrolysis

The mass of substance deposited during electrolysis

The mass of a substance produced at an electrode during electrolysis is proportional to:
■The time over which a constant electric current pass
■The strength of the electric current.



Combining current and time, we get the relationship:
The mass of a substance during electrolysis is proportional to the electricity passing through the electrolyte, expressed in Faraday units, which represent the electric charge carried by 1 mole of electrons or ions.
Its value is 96 500Cmol–1 (to 3 significant figures).

During the electrolysis of silver nitrate solution, silver is deposited at the cathode:

$Ag^+ + e^- \longrightarrow Ag$ 1

1 mol 1 mol 1 mol

1 Faraday of electricity (96 500C) is required to deposit 1 mole of silver.

During the electrolysis of copper (II) sulfate solution, copper is deposited at the cathode:

$Cu^{2+} + 2^{e-} \longrightarrow Cu$ 1

1mol 2mol 1 mol

The equation shows that 2 moles of electrons are needed to produce 1 mole of copper from Cu2+ ions. So, it requires 2 Faradays of electricity (2 × 96 500C) to deposit 1 mole of copper.

During the electrolysis of molten sodium chloride, chlorine is produced at the anode:

$2Cl^- \longrightarrow Cl^2 + 2e^-$

2 mol 1mol 1 mol

During the electrolysis of an aqueous solution of sulfuric acid or aqueous sodium sulfate, oxygen is produced at the anode:

$4OH^-(aq)\ O2(g) + 2H2O(l) + 4e^-$

The equation reveals that forming 1 mole of oxygen gas from 4 moles of OH-ions releases 4 moles of electrons, requiring 4 Faradays of electricity.

Calculating the amount of substance produced during electrolysis

We can use the value of F to calculate:

- The mass of substance deposited at an electrode
- The volume of gas produced at an electrode.

Calculating the Avogadro constant by an electrolytic method

The Avogadro constant, L, is the number of specified particles in 1 mole. We can use an electrolytic method to find a value for the Avogadro constant by calculating the charge associated with 1 mole of electrons.

$$L = \frac{\text{charge on 1 mole of electrons}}{\text{charge on 1 electron}}$$

We can calculate the charge on the electron by experiment. The results show us that the charge on the electron is approximately 1.60 × 10–19C.

Finding the charge on 1 mole of electrons

The charge on 1 mole of electrons can be found in a simple electrolytic experiment. The apparatus for this is shown in Figure 20.3.

The procedure is:

- Weigh the pure copper anode and pure copper cathode separately

- Arrange the apparatus as shown in Figure 20.3; the variable resistor is used to keep the current constant

- Pass a constant electric current for a measured time interval

Finding the charge on 1 mole of electrons (continued)

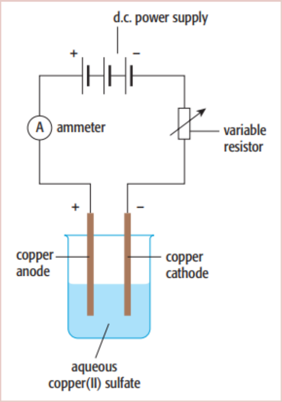


Figure 20.3 Apparatus for calculating the mass of copper deposited during the electrolysis of aqueous copper(II) sulfate.

Electrode potentials

Introducing electrode potentials

A redox equilibrium exists between two chemically related species that are in different oxidation states. There are two opposing reactions in this equilibrium.

- Metal atoms from the rod entering the solution as metal ions. This leaves electrons behind on the surface of the rod.
- Ions in solution accept electrons from the metal rod and are deposited as metal atoms on the surface of the rod.

The redox equilibrium is established when the rate of electron gain equals the rate of electron loss. For unreactive metals such as copper, if this equilibrium is compared with the equilibrium set up by other metals, the equilibrium set up by copper lies further over to the right.

Equilibrium positions vary for metal combinations in ion solutions, as an electric potential is established between the metal and ions, but this potential cannot be directly measured.

We call this value the **electrode potential**, E. Electrode potential is measured in volts. The system we use for comparison is the standard hydrogen electrode

It is thought that the absolute electrical potentials that we cannot measure are caused by the formation of an electrical double layer when an element is placed in a solution of its ions.

The standard hydrogen electrode

The standard hydrogen electrode is one of several types of half cells that can be used as reference electrodes. Figure 20.5 shows a standard hydrogen electrode.
This electrode consists of:

- Hydrogen gas at 101kPa pressure, in equilibrium with
- H^+ ions of concentration $1.00 mol dm^{-3}$
- A platinum electrode covered with platinum black in contact with the hydrogen gas and the H^+ ions.

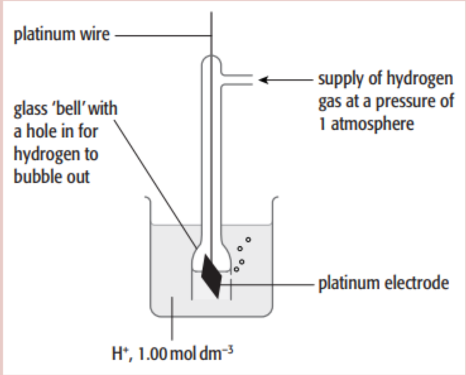


Figure 20.5 The standard hydrogen electrode.

The platinum black electrode, finely divided, facilitates quick equilibrium between hydrogen gas and H+ ions in solution. It is inert, preventing reaction involvement. Standard electrode potential E^{θ} values are measured relative to this electrode.

The half-equation for the hydrogen electrode can be written:

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

or

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

The way that the half-equation is balanced makes no difference to the value of E^{θ}. The equation does not affect the tendency for the element to gain electrons.

Electrode potential and redox reactions

Electrode potential values give us an indication of how easy it is to reduce a substance.
Note that:

- By convention, the electrode potential refers to the reduction reaction. So, the electrons appear on the left-hand side of the half-equation.
- The more positive (or less negative) the electrode potential, the easier it is to reduce the ions on the left. So the metal on the right is relatively unreactive and is a relatively poor reducing agent.
- The more negative (or less positive) the electrode potential, the more difficult it is to reduce the ions on the left.

So, the metal on the right is relatively reactive and is a relatively good reducing agent.

Combining half-cells
To measure the electrode potential relating to the half-equation.
$Cu^{2+(}$aq) + 2^{e-} → Cu(s)
we place a pure copper rod in a solution of $Cu^{2+(}$aq) ions
We use the following standard conditions to make the half-cell:
- The Cu^{2+} (aq) ions have a concentration of 1.00moldm^{-3}
- The temperature is 25 °C (298K)
- The copper rod must be pure

If we connect two half-cells, we have made an electrochemical cell.
Half-cells are connected using:
Electrons flow through a circuit connecting metal rods in half-cells to a high-resistance voltmeter, varying from metals with negative or positive electrode potential to metals with positive or negative electrode potential.

A salt bridge is a crucial component in electrical circuits, facilitating the movement of ions between two half-cells, while preventing the movement of electrons.
A salt bridge is a device that connects two or more surfaces by absorbing a substance, such as potassium nitrate, through a porous material.

Standard electrode potential

Standard conditions are essential when comparing electrode potentials, as the equilibrium position of a reaction can be influenced by reagent concentration, temperature, and gas pressure.
These are:
- Concentration of ions at 1.00moldm^{-3}
- A temperature of 25°C (298K)
- Any gases should be at a pressure of 1 atmosphere (101kPa)
- The value of the electrode potential of the half-cell is measured relative to the standard hydrogen electrode

Under these conditions, the electrode potential we measure is called the standard electrode potential. This has the symbol, E^{θ}. It is spoken of as 'E standard'.

Measuring standard electrode potentials

There are three main types of half-cells whose E^{θ} value can be obtained when connected to a standard hydrogen electrode:
- Metal/metal ion half-cell
- Non-metal/non-metal ion half-cell
- Ion/ion half-cell.

Half-cells containing metals and metal ions

Figure 20.8 demonstrates measuring the E^{θ} value for a Cu^{2+} /Cu half-cell, connected to a standard hydrogen electrode and measuring the voltage at +0.34V. The two half-equations are:

$$Cu^{2+}(aq) + 2e^{-} \rightleftharpoons Cu(s) \qquad E^{\ominus} = +0.34\,V$$

$$H^{+}(aq) + e^{-} \rightleftharpoons \tfrac{1}{2}H_2(g) \qquad E^{\ominus} = 0.00\,V$$

- The $E^{\ominus}$ values show us that Cu^{2+} ions are easier to reduce than H^{+} ions (they have a more positive $E^{\ominus}$ value).
- Cu^{2+} ions are more likely to gain electrons than H^{+} ions.
- So Cu^{2+} ions will accept electrons from the H^{+}/H_2 half-cell and H_2 will lose electrons to the Cu^{2+}/Cu half-cell.

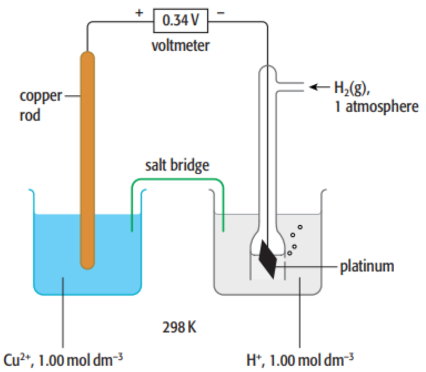


Figure 20.8 Measuring the standard electrode potential of a Cu^{2+}/Cu half-cell.

Figure 20.9 demonstrates measuring the E $^{\theta}$ value for a Zn^{2+} /Zn half-cell with -0.76V voltage, with zinc as the negative terminal and hydrogen electrode as the positive terminal. The two half-equations are:

$$H^+(aq) + e^- \rightleftharpoons \tfrac{1}{2}H_2(g) \qquad E^\ominus = 0.00\,V$$

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad E^\ominus = -0.76\,V$$

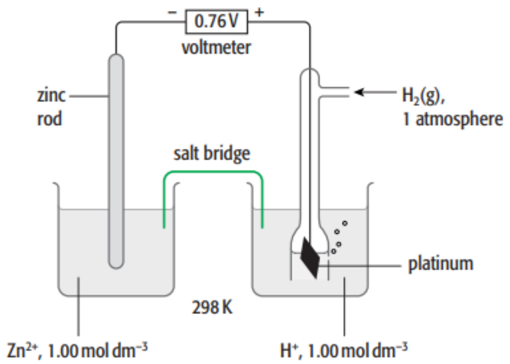


Figure 20.9 Measuring the standard electrode potential of a Zn^{2+}/Zn half-cell.

- The $E^\ominus$ values show us that Zn^{2+} ions are more difficult to reduce than H^+ ions (they have a more negative $E^\ominus$ value).
- Zn^{2+} ions are less likely to gain electrons than H^+ ions.
- So Zn will lose electrons to the H^+/H_2 half-cell and H^+ ions will gain electrons from the Zn^{2+}/Zn half-cell.

From these two examples, we can see that:

- Reduction takes place at the positive terminal of the cell. For example, in the Zn^{2+}/Zn; H^+/H_2 cell:

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

- Oxidation takes place at the negative terminal of the cell. For example, in the Zn^{2+}/Zn: H^+/H_2 cell:

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

Half-cells containing non-metals and non-metal ions

In half-cells that do not contain metal, electrical contact with the solution is made by using platinum wire or platinum foil as an electrode. The redox equilibrium is established at the surface of the platinum. The platinum electrode is inert so plays no part in the reaction. Platinum must be in contact with both the element and the aqueous solution of its ions.

Figure 20.11 displays a Cl^2/Cl^- half-cell connected to a hydrogen electrode, with a voltage of +1.36V, forming the positive terminal and the negative terminal. The two half-equations are:

$$\tfrac{1}{2}Cl_2(g) + e^- \rightleftharpoons Cl^-(aq) \qquad E^\ominus = +1.36\,V$$

$$H^+(aq) + e^- \rightleftharpoons \tfrac{1}{2}H_2(g) \qquad E^\ominus = 0.00\,V$$

- The $E^\ominus$ values show us that Cl_2 molecules are easier to reduce than H^+ ions (they have a more positive $E^\ominus$ value).
- Cl_2 molecules are more likely to gain electrons than H^+ ions.
- So Cl_2 molecules will gain electrons from the $H^+/\tfrac{1}{2}H_2$ half-cell and H_2 molecules will lose electrons to the $\tfrac{1}{2}Cl_2/Cl^-$ half-cell.

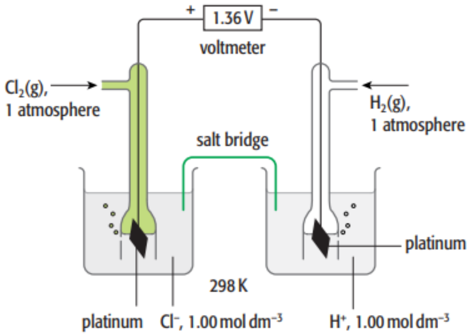


Figure 20.11 Measuring the standard electrode potential of a Cl_2/Cl^- half-cell.

Half-cells containing ions of the same element in different oxidation states

Half-cells, formed by a mixture of Fe^{3+} and Fe^{2+} ions, can contain different oxidation states from the same element, with a concentration of 1.00moldm$^{-3.}$

The voltage of this half-cell is +0.77V

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \qquad E^\ominus = +0.77\,V$$

Some reactions involve several ionic species. For example:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$$

The H^+ ions are included because they are essential for the conversion of MnO_4 – (manganate (VII) ions) to Mn^{2+} ions. So, the half-cell contains:

■ 1.00moldm^{-3} $MnO^{4-(}$aq) ions
■1.00moldm^{-3} $Mn_{2+(}$aq) ions
■1.00moldm^{-3} H^+(aq) ions.

Figure 20.14 shows the set-up of a cell used to measure the the standard electrode potential of the Mn^{O4-}/Mn^{2+} half-cell.

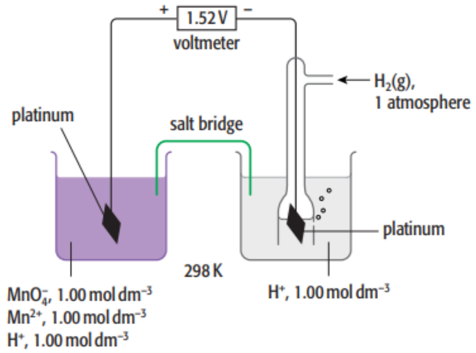


Figure 20.14 Measuring the standard electrode potential of the MnO_4^-/Mn^{2+} half-cell.

Using E —O values

Using E —O values to predict cell voltages

We can use E^θ values to calculate the voltage of an electrochemical cell made up of two half-cells, even when neither of them is a standard hydrogen electrode. The voltage measured is the difference between the E^θ values of the two half-cells. we call this value the **standard cell potential.**

For the electrochemical cell shown in Figure 20.15, the two relevant half-equations are:

$$Ag^+(aq) + e^- \rightleftharpoons Ag(s) \qquad E^\ominus = +0.80\,V$$

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad E^\ominus = -0.76\,V$$

The voltage of this cell is +0.80 – (–0.76) = +1.56V (Figure 20.16). Note that to calculate the cell voltage, we always subtract the less positive E^θ value from the more positive E^θ value.

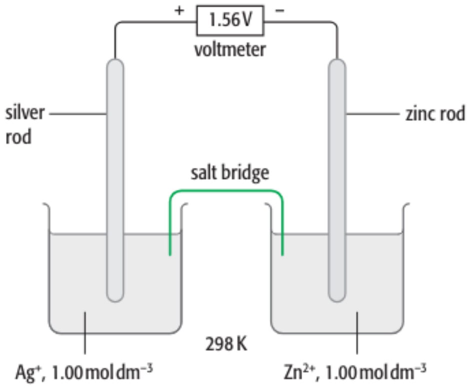


Figure 20.15 An Ag^+/Ag, Zn^{2+}/Zn electrochemical cell.

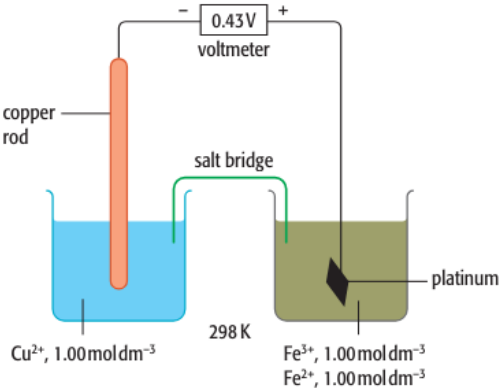


Figure 20.17 An Cu^+/Cu, Fe^{3+}/Fe^{2+} electrochemical cell.

For the electrochemical cell shown in Figure 20.17, the relevant half-equations are,

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \qquad E^\ominus = +0.77\,V$$

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E^\ominus = +0.34\,V$$

The cell's voltage is +0.43V, with the Fe^{3+} /Fe^{2+} half-cell being the positive pole and the Cu^{2+} /Cu half-cell being the negative pole.

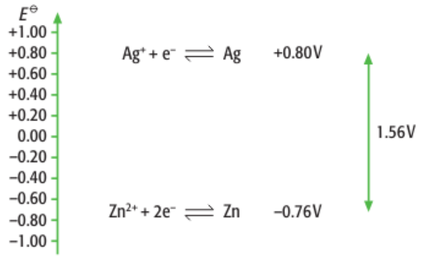


Figure 20.16 The difference between +0.80 V and −0.76 V is +1.56 V.

E $^{\theta}$ values and the direction of electron flow

We can deduce the direction of electron flow in the wires in the external circuit by comparing the E —O values for the two half-cells which make up the electrochemical cell. For example, in Figure 20.15 these voltages are:

$$Ag^+(aq) + e^- \rightleftharpoons Ag(s) \qquad E^{\ominus} = +0.80\,V$$

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad E^{\ominus} = -0.76\,V$$

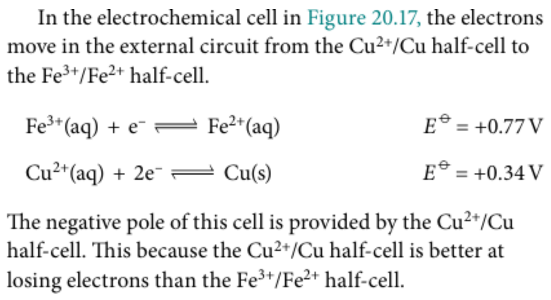
The relative values of these voltages tell us that Zn2+ ions are more difficult to reduce than Ag^+ ions. So:

■Zn metal will lose electrons to the Ag^+ /Ag half-cell

■Ag+ ions will accept electrons from the Zn^{2+} /Zn half-cell.

The electrons move through the wires in the external circuit. They do not travel through the electrolyte solution.

So, the electron flow is from the Zn^{2+} /Zn half-cell to the Ag+/Ag half-cell. In other words, the flow is from the negative pole to the positive pole. It may help you to remember that the more positive pole attracts the negative electrons



In the electrochemical cell in Figure 20.17, the electrons move in the external circuit from the Cu^{2+}/Cu half-cell to the Fe^{3+}/Fe^{2+} half-cell.

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq) \qquad E^{\ominus} = +0.77\,V$$

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E^{\ominus} = +0.34\,V$$

The negative pole of this cell is provided by the Cu^{2+}/Cu half-cell. This because the Cu^{2+}/Cu half-cell is better at losing electrons than the Fe^{3+}/Fe^{2+} half-cell.

Using E —O values to predict if a reaction will occur

Standard electrode potential values, E^{θ} give us a measure of how easy or difficult it is to oxidize or reduce a species. We can compare the oxidizing and reducing powers of elements and ions by comparing the E^{θ} values for their half-reactions.

■ The more positive the value of E^{θ} the greater the tendency for the half-equation to proceed in the forward direction.

■The less positive the value of E^{θ} the greater the tendency for the half-equation to proceed in the reverse direction.

■The more positive the value of E^{θ} the easier it is to reduce the species on the left of the half-equation.

■The less positive the value of E^{θ} the easier it is to oxidize the species on the right of the half-equation. We can make an electrochemical cell from the two half-cells:

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E^{\ominus} = +0.34\,V$$

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad E^{\ominus} = -0.76\,V$$

Cu^{2+} has a greater tendency to gain electrons than Zn^{2+} so the chemical reaction that proceeds in this half-cell is in the forward direction:

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

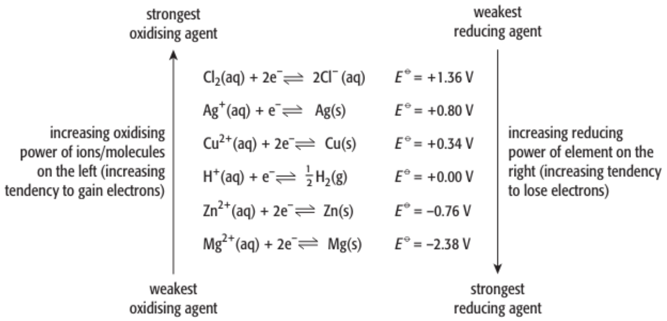


Figure 20.18 Standard electrode potentials for some oxidising and reducing agents.

E^{θ} values and oxidizing and reducing agents

Look back at Figure 20.18 (page 286). Note the following as the values of E —O for each of these reduction
reactions get more negative.

■The species on the left of the equation become weaker oxidizing agents. They accept electrons less readily.

■The species on the right of the equation becomes strong

Cu will not reduce Zn^{2+} ions to Zn. So how can we reduce Zn^{2+} ions? The answer is to react the Zn^{2+} ions with a stronger reducing agent, which should have an $E^{\ominus}$ value more negative than the $E^{\ominus}$ value for Zn^{2+}/Zn. In Figure 20.18 we see that the half-equation Mg^{2+}/Mg has a more negative $E^{\ominus}$ value. So Mg is a suitable reducing agent.

$$Zn^{2+}(aq) + e^{-} \rightleftharpoons Zn(s) \qquad E^{\ominus} = -0.76\,V$$

$$Mg^{2+}(aq) + 2e^{-} \rightleftharpoons Mg(s) \qquad E^{\ominus} = -2.38\,V$$

How does the value of E^{θ} vary with ion concentration?

The equilibrium reactions' positions are influenced by changes in concentration, temperature, and pressure, and redox equilibriums are similar. The electrode potential, represented by the symbol E, changes under nonstandard conditions. What happens to the electrode potential when we change the concentration of ions in a half-cell? Let us take an example of a metal/metal ion equilibrium:

$$Zn^{2+}(aq) + e^{-} \rightleftharpoons Zn(s) \qquad E^{\ominus} = -0.76\,V$$

- If $[Zn^{2+}]$ is greater than 1.00 mol dm^{-3}, the value of E becomes less negative / more positive (for example −0.61 V).
- If $[Zn^{2+}]$ is less than 1.00 mol dm^{-3}, the value of E becomes more negative / less positive (for example −0.80 V).

We can apply Le Chatelier's principle to redox equilibria. If we increase the concentration of the species on the left of the equation, the position of equilibrium will shift to the right. So, the value of E becomes more positive / less negative. If two different ions are present in the half-cell, we must consider both ions

The Nernst equation

If we consider a cell made up of a silver/silver ion electrode and a copper/copper (II) ion electrode, the reaction taking place is:

$$Cu(s) + 2Ag^{+}(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s) \quad E^{\ominus} = +0.46\,V$$

standard conditions and change the concentration of the silver ions, we obtain the graph shown in Figure 20.23. Note that we have plotted the value of E_{cell} (non-standard conditions for the cell as a whole) against the logarithm of the silver ion concentration.

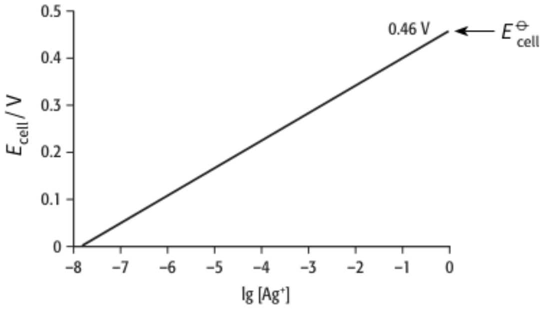


Figure 20.23 Increasing the concentration of silver ions in the cell reaction $Cu(s) + 2Ag^{+}(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$ makes the value of E_{cell} more positive.

The effect of concentration and temperature on the value of E_{cell} can be deduced using the Nernst equation. For a given electrode, e.g. a $Cu(s)/Cu^{2+}(aq)$ electrode, the relationship is:

$$E = E^{\ominus} + \frac{RT}{zF}\ln\frac{[\text{oxidised form}]}{[\text{reduced form}]}$$

Feasibility predictions based on E^{θ} don’t always work!

E^{θ} values indicate the feasibility of a reaction, but they don't guarantee quick or reverse reactions. Some reactions, like zinc's lack of reactivity with cold water, occur slowly due to H+ ions. The relevant half-equations are:

$$H^+ + e^- \rightleftharpoons \tfrac{1}{2}H_2(g) \qquad E^{\ominus} = 0.00\,V$$

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad E^{\ominus} = -0.76\,V$$

E^{θ} values predict a reaction, but the rate of zinc-water reaction is slow, determining the lack of reactivity, rather than the E^{θ} value.

Cells and batteries

The variety of cells

Recent developments in electrochemical cells cater to specific functions, with smaller cells producing low voltage, while larger batteries offer higher voltage but require more space.

- Whether or not the cell can be recharged
- The size and mass of the cell
- The voltage of the cell
- The nature of the electrolyte
- How long the cell can deliver its maximum voltage
- The cost of the cell.

Rechargeable cells

Primary cells continue to redox reactions until reactants reach low concentrations, causing cell voltage to decline. Secondary cells, or storage cells, can be recharged by passing an electric current, like a car battery with plates of lead and lead (IV) oxide in sulfuric acid.

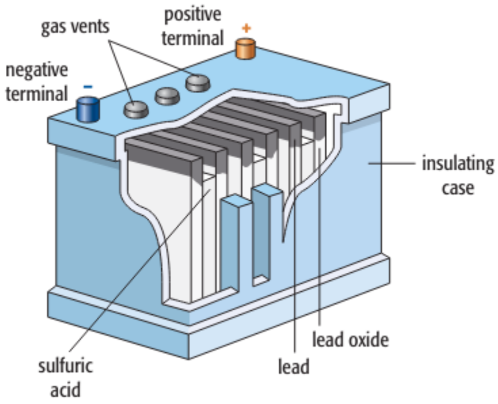


Figure 20.24 The storage cell used in a car.

Improved batteries for electric vehicles have been developed.

- Nickel-cadmium cells are smaller and have a lower mass than lead-acid cells but they give a lower voltage. They do not ‘run down’ as quickly.
- Aluminum-air–air batteries are lightweight and Produce a higher voltage than a lead–acid battery. They are expensive and are not true secondary cells because the aluminium anode has to be replaced from time to time.

Solid state cells

In recent years, primary cells have been developed with improved voltage and reduced size. Cells the size of a large buttons are used in heart pacemakers, hearing aids and other medical uses as well as in watches and calculators. They have several advantages:

- They are lightweight and small
- They give a high voltage, for example, 3.0V
- They give a constant voltage over time
- They do not contain liquids or paste, so they do not leak.

Commonly used ‘button’ cells use lithium or zinc as the negative pole and iodine, manganese (IV) oxide or silver oxide as the positive pole.

Figure 20.25 Button cells like these are used to power watches and hearing aids.

Hydrogen–oxygen fuel cells

Fuel cells are electrochemical cells where fuel releases electrons and oxygen gains electrons, replacing petrol in vehicles. They produce voltage for electric motors. Hydrogen-oxygen fuel cells are one type, using platinum-coated electrodes to bubble hydrogen and oxygen gas, allowing half-reactions.

Figure 20.26 Fuel cells may eventually replace petrol and diesel engines in cars.

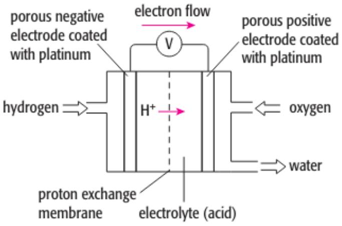


Figure 20.27 A hydrogen–oxygen fuel cell.

There are several limitations to hydrogen-oxygen fuel cells.

- High cost: the materials used to make the electrodes and membrane are expensive.
- Manufacturing of fuel cells involves the production of toxic by-products.
- Storage of hydrogen: high-pressure tanks are needed to store enough fuel. At present refueling has to be done more often compared with a petrol engine.
- Manufacturing hydrogen: the hydrogen needed for fuel cells can only be produced cheaply by using fossil fuels.
- Fuel cells do not work well at low temperatures: if the temperature falls much below 0°C, the fuel cell ‘freezes.

More about electrolysis

During electrolysis:

- Cations (positive ions) move towards the cathode where they gain electrons; the gain of electrons is a reduction
- Anions (negative ions) move towards the anode where they lose electrons; loss of electrons is oxidation.

Electrolysis of molten electrolytes

When pure molten ionic compounds containing two simple ions are electrolyzed, a metal is formed at the cathode and a non-metal at the anode.

Electrolysis of aqueous solutions

Aqueous solutions of electrolytes contain more than one cation and more than one anion. So – we have to ask, which ions are discharged (changed into atoms or molecules) during the electrolysis of aqueous solutions? Among other things this depends on:

- The relative electrode potential of the ions
- The concentration of the ions

Electrolysis products and electrode potentials

When an aqueous ionic solution is electrolyzed using inert electrodes, there is usually only one product obtained at each electrode. The ease of discharge of cations at the cathode is related to their electrode potentials. Figure 20.28 shows some half-reactions and their electrode potentials.

$E^\ominus$/ V	
+0.80	$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$
+0.34	$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$
0.00	$H^+(aq) + e^- \rightleftharpoons \frac{1}{2}H_2(g)$
−0.13	$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$
−0.76	$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$
−2.38	$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$
−2.71	$Na^+(aq) + e^- \rightleftharpoons Na(s)$

↑ increasing ease of discharge of cation at cathode

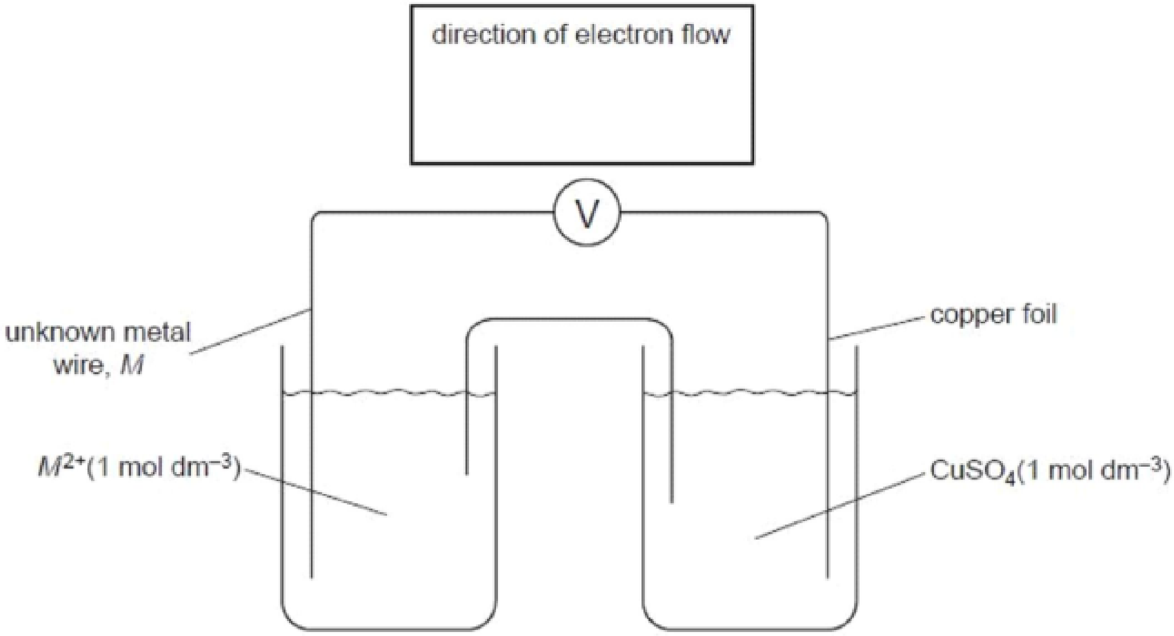
Figure 20.28 The ease of discharge of ions at a cathode in electrolysis is related to the electrode potential of the ions.

Electrolysis products and solution concentration

Electrolysis of aqueous solutions results in a mixture of chlorine and oxygen at the anode. Ions are rarely present at concentrations of 1.00moldm^{-3}, and the value of E changes with the ion's concentration. For example, when electrolyzing a concentrated solution of sodium chloride, chloride ions are discharged in preference to hydroxide ions. However, when electrolyzing an extremely dilute solution, oxygen is formed instead of chlorine, due to the lower concentration of Cl$^-$ ions.

Revision questions

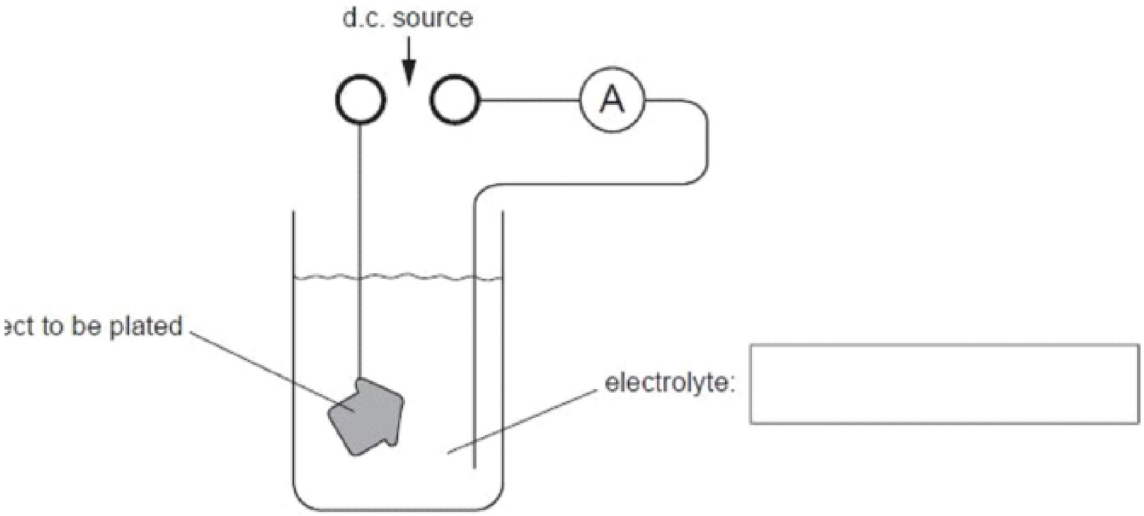
1) (a) What do you understand by the term standard electrode potential?
(b) The following cell was set up between a copper electrode and an unknown metal electrode M^{2+}(aq)/M(s). The standard cell potential was found to be 0.76V, and the copper foil was the positive electrode.



(i) Use the Data Booklet to calculate the standard electrode potential of the M^{2+} (aq)/M(s) system.
(ii) Draw an arrow over the voltmeter symbol in the above diagram to show the direction of electron flow through the voltmeter.
(iii) Predict the outcomes of the following situations. Describe what you might see and write ionic equations for any reactions that occur.
1. A rod of metal M is dipped into a solution of 1 mol dm^{-3} $CuSO_4$.
2. Dilute sulphuric acid is added to a beaker containing a powdered sample of metal M.

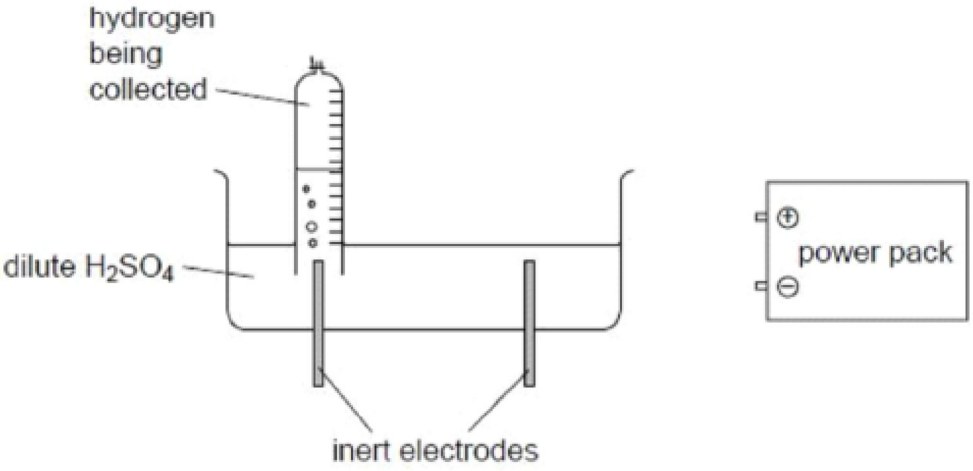
(c) Because of its increased scarcity, cheaper copper ornaments are no longer made from the solid metal, but from iron that has been copper-plated.

(i) Complete the following diagram showing the setup for a copper electroplating process. Show clearly the polarity (+/-) of the power source and suggest a suitable electrolyte.



(ii) A current of 0.500 A is passed through the electroplating cell. Calculate the time required to deposit a mass of 0.500 g of copper onto the ornament.

2) A student decided to determine the value of the Faraday constant by an electrolysis experiment. The following incomplete diagram shows the apparatus that was used.



(a) (i) Apart from connecting wires, what two additional pieces of equipment are needed for this experiment?
(ii) Complete the diagram, showing additional equipment connected in the circuit, and showing the powerpack connected to the correct electrodes.
(iii) List the measurements the student would need to make to use the results to calculate a value for the Faraday constant.

(b) (i) Using an equation, state the relationship between the Faraday constant, F, the Avogadro constant, L, and the charge on the electron, e.
(ii) The value the student obtained was: 1 Faraday = 9.63 x 104 Coulombs

Use this value and your equation in (b)(i) to calculate the Avogadro constant (take the charge on the electron to be 1.60×10^{-19} Coulombs)

3) Zinc chloride is one of the most important compounds of zinc. It is used in dry cell batteries, as a flux for soldering and tinning, as a corrosion inhibitor in cooling towers and in the manufacture of rayon.

(a) Draw a fully labelled diagram to show how you could use a standard hydrogen electrode to measure the standard electrode potential, E^{θ}, of zinc.

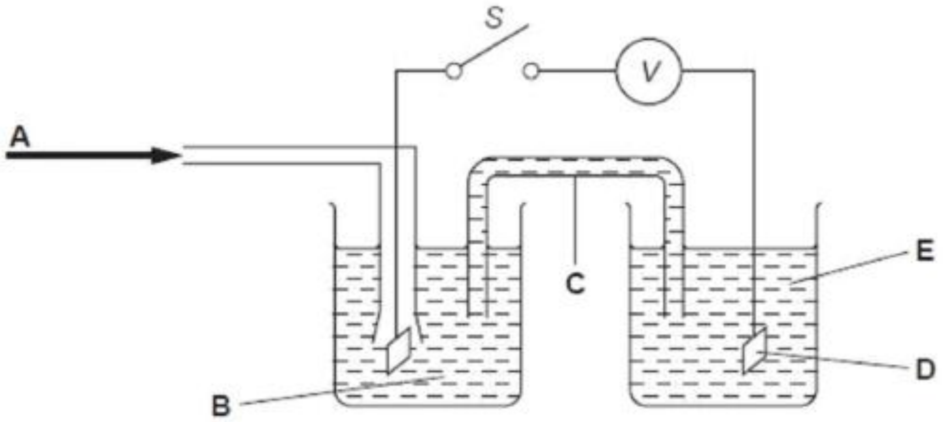
(b) The electrolysis of zinc chloride can give different electrode products, depending on the conditions used. Suggest the products formed at each electrode in the following cases. One space has been filled in for you.

conditions	product at anode	product at cathode
$ZnCl_2$(l)	***chlorine***	
$ZnCl_2$(concentrated aqueous)		
$ZnCl_2$(dilute aqueous)		

4)Chlorine gas and iron (II) ions react in aqueous solution.

Cl_2+ $2Fe^{2+}$ → 2ct + $2Fe^{3+}$

(a) The following diagram shows the apparatus needed to measure the Ell for the above reaction.



(i) In the spaces below, identify what the five letters A - E in the above diagram represent.

(ii) Use the Data Booklet to calculate the E 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.

(b) Iron (III) chloride readily dissolves in water.

$FeCl_3$(s) Fe^{3+} (aq) + $3C^{1-}$ (aq)

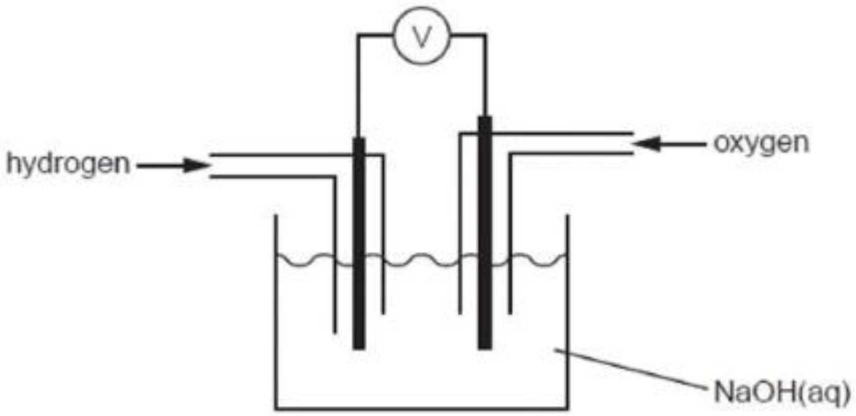
species	$\Delta H_f^{\ominus}$/kJmol^{-1}
$FeCl_3$(s)	–399.5
Fe^{3+}(aq)	–48.5
Cl^-(aq)	–167.2

(i) Use the following data to calculate the standard enthalpy change for this process.
(ii) An iron (III) chloride solution dissolves 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 Booklet to calculate the E^θ for the reaction.

5)(a) Describe the observations you would make when concentrated sulfuric acid is added to separate portions of NaC1(s) and NaBr(s). Write an equation for each reaction that occurs.
(b) By quoting relevant E data from the Data Booklet, explain how the observations you have described above relate to the relative oxidizing power of the elements.

(c) By referring to relevant E data choose a suitable reagent to convert Br2 into Br-. Write an equation and calculate the E for the reaction.

6)Although standard electrode potentials are measured for solutions where the concentrations of ions are 1.0 mol dm^3, cells used as sources of battery power tend to operate with more concentrated solutions. This question concerns the electrode reactions involved in the hydrogen-oxygen fuel cell and the lead-acid car battery.
(a) In the hydrogen-oxygen fuel cell, H_2(g) and O_2(g) are fed onto two inert electrodes dipping into NaOH(aq).



The following reactions take place.

left hand electrode (cathode): $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$

right hand electrode (anode): $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

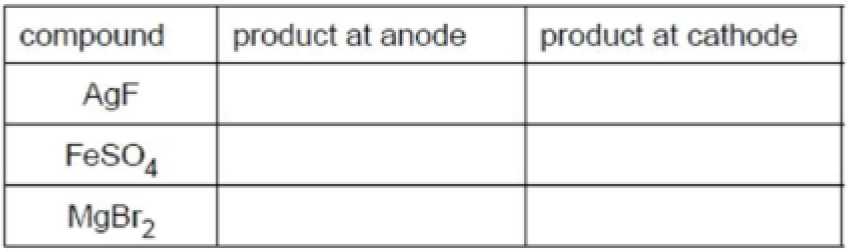
(i) Use the Data Booklet to calculate E $^{\theta}_{cell}$ for this reaction.
(ii) Construct an equation for the overall reaction.
(iii) By using one of the phrases more positive, more negative or no change, deduce the effect of increasing $[OH^-(aq)]$ on the electrode potential of
(iv) Hence deduce whether the overall E $^{\theta}_{cell}$ is likely to increase, decrease or remain the same, when $[OH^-(aq)]$ increases. Explain your answer.
(v) Suggest one other reason why a high [NaOH(aq)] is used in the fuel cell.

7)(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, 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.

(i) Draw a diagram of a 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= 52.243g
the final mass of copper cathode= 52.542g
(ii) Use these data and relevant information from the Data Booklet to calculate a value of L to 3 significant figures.
(c) Use relevant information from the Data Booklet to identify the substances formed at the anode and the cathode when aqueous solutions of the following compounds are electrolyzed.



compound	product at anode	product at cathode
AgF		
$FeSO_4$		
$MgBr_2$		

8)(a) What is meant by the term standard electrode potential, SEP?

(b) Draw a fully labelled diagram of the apparatus you could use to measure the SEP of the Fe^{3+} /Fe^{2+} electrode.

9)(a) (i) With the aid of a fully labelled diagram, describe the standard hydrogen electrode.
(ii) Use the Data Booklet to calculate the standard cell potential for the reaction between Cr^{2+} ions and $Cr_2O_7,^{2-}$ ions in acid solution and construct a balanced equation for the reaction.
iii) Describe what you would see if a blue solution of Cr^{2+} ions was added to an acidified solution of $Cr_2O_7,^{2-}$ ions until the reaction was complete.