24 Electrochemistry

Electrolysis

- Electrochemistry involves both using chemical reactions to generate electricity and using electricity to bring about chemical reactions. You may have already seen examples of this in the chemical industry for GCSE.
- We will begin by looking at electrolysis. For A Level you may be asked to predict the identity of substances made during electrolysis knowing the state (molten or aqueous) and concentration of the electrolyte, and the position of the element in the redox series (its electrode potential).

Calculating quantities of materials used or produced during electrolysis

Like all chemical reactions, it is possible to calculate quantities of materials used or produced in such a process. In the case of electrolysis you can work out, for example, how many electrons are needed to produce one atom of aluminium:

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

The quantity of electricity needed to make 1 mole of a product depends on the number of electrons needed to make each atom, the charge on an electron and the number of atoms involved. The magnitude of the charge per mole of electrons is called the Faraday constant and is usually quoted as 96 500 C mol^{-1}. This is expressed as:

$$F = Le$$

where L is the Avogadro constant and e is the charge on the electron.

Calculating charge passed during electrolysis

In an examination you might also be asked to calculate the quantity of charge passed during electrolysis, or the mass and/or volume of a substance made during the process. Let us look at how you might tackle this.

WORKED EXAMPLE

What mass of copper is produced at the cathode when 2.40 A are passed through a solution of copper(II) sulfate for 25 minutes?

Answer

First, calculate the number of coulombs of charge passed. Remember that charge equals current in amps multiplied by time in seconds:

$$2.40 \times 25 \times 60 = 3600\ \text{C}$$

Next, calculate how many moles of electrons this corresponds to:

$$\frac{3600}{96\,500} = 3.73 \times 10^{-2}\,\text{mol}$$

Because copper(II) ions have a charge of +2 this corresponds to:

$$\frac{3.73 \times 10^{-2}}{2}\,\text{mol of copper}$$

So the mass of copper produced is:

$$\frac{3.73 \times 10^{-2}}{2} \times 63.5 = 1.18\,\text{g}$$

In the electrolysis of a solution of sodium sulfate, Na_2SO_4, or sulfuric acid, H_2SO_4, the product at the cathode is hydrogen gas. Instead of using mass, you can use the volume as a fraction of the molar volume of a gas, 24 dm^3.

A value for the Avogadro constant can be determined using electrolysis. This requires the measurement of the mass of an element, such as copper, produced in a fixed period of time at a constant known current, to be measured as accurately as possible. Knowing the charge on the copper(II) ion you can then use $F = Le$ to determine L, the Avogadro constant.

Predicting the products of electrolysis

Some exam questions may ask you to predict what substances are liberated at a given electrode. To answer this, check if the electrolysis is taking place in the molten salt or in an aqueous solution, and then consider the electrode potentials and concentrations of the ions.

- If it is a molten salt there can only be one element discharged at each electrode.
- If it is an aqueous solution it is possible for hydrogen to be discharged at the cathode and oxygen at the anode:

$$4H^+ + 4e^- \rightarrow 2H_2(g) \qquad E^\ominus = 0.00\,V$$

$$4OH^- - 4e^- \rightarrow 2H_2O(l) + O_2(g) \qquad E^\ominus = -0.40\,V$$

- To decide which ions are discharged, compare $E^\ominus$ for the half-cell reactions above with those of the other ions in solution.

Consider the electrolysis of a concentrated solution of sodium chloride. Hydrogen is produced at the cathode because hydrogen ions accept electrons more easily than sodium ions. On the other hand, chlorine is produced at the anode because chloride ions are present in a higher concentration than hydroxide ions.

NOW TEST YOURSELF

1 Suppose we were electrolysing a dilute solution of potassium sulfate.
   a What would be produced at the anode?
   b What would be produced at the cathode?
   c Which ions would remain in solution?

Electrode potentials

Now let us look at chemical reactions generating an electric current (electrode potentials).

It is important that you learn two definitions linked to electrode potentials.

A **standard hydrogen electrode** is shown in Figure 24.1.

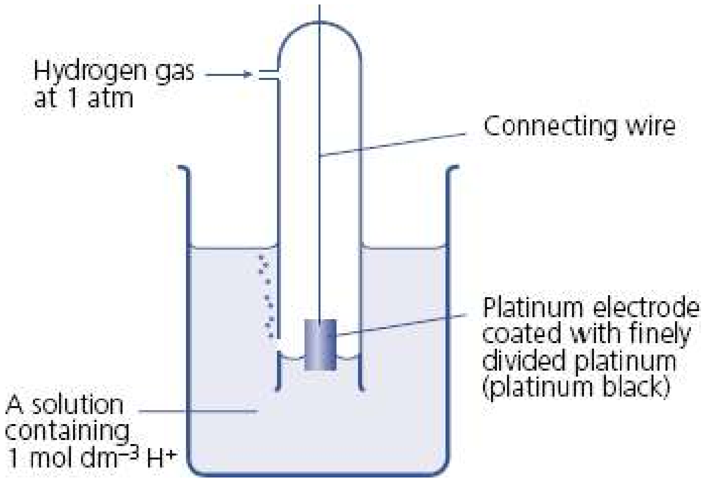

Figure 24.1 A standard hydrogen electrode

STUDY TIP

It is important to be able to draw a standard hydrogen electrode in an exam.

In Figure 24.2 you can see how the **standard electrode potential** of another electrode can be measured using the hydrogen electrode.

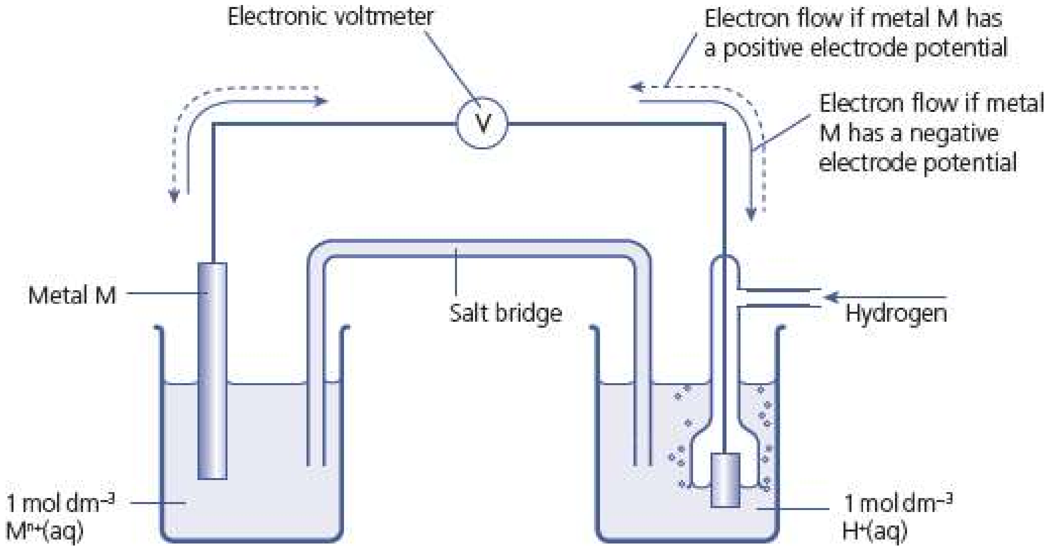

Figure 24.2 Measuring a standard electrode potential

KEY TERM

A **standard electrode (redox) potential** is defined as the electrode potential measured under standard conditions (temperature 298 K, 1 atmosphere pressure, 1 mole of the redox participants of the half-reaction) against a standard hydrogen electrode.

A **standard cell potential** is the potential produced when two standard electrodes are connected to form a cell such as that in Figure 24.3.

KEY TERM

Standard cell potential is the potential produced when two standard electrodes are connected to form a cell.

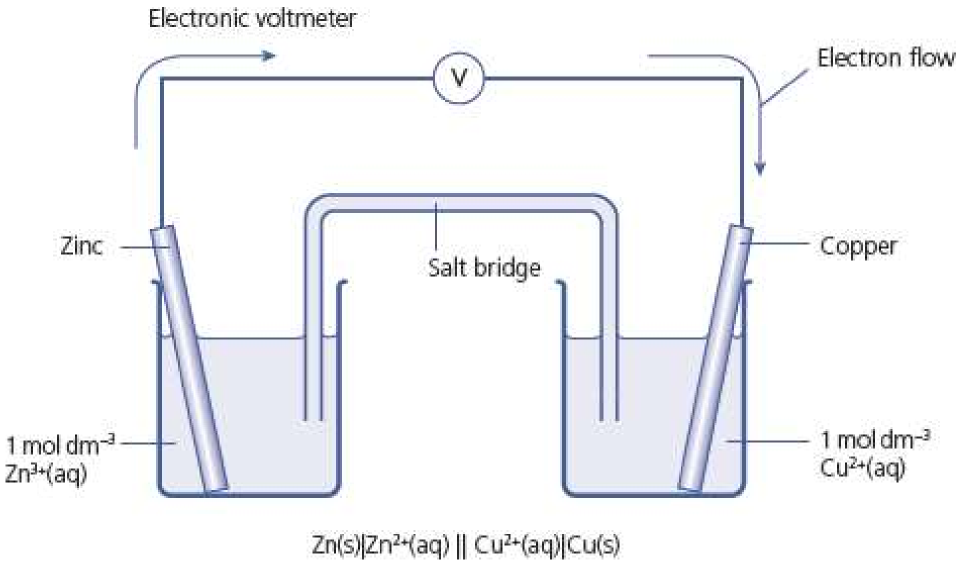

Figure 24.3 Apparatus for determining a standard cell potential

Calculating the cell potential

A cell potential has a contribution from the anode, which is a measure of its ability to lose electrons – its **oxidation potential**. The cathode has a contribution based on its ability to gain electrons – its **reduction potential.** The cell potential can then be written as:

$$E_{\text{cell}} = \text{oxidation potential} + \text{reduction potential}$$

As with oxidation numbers, when calculating an overall cell potential, it helps to work using a linear scale from negative to positive as shown in Figure 24.4.

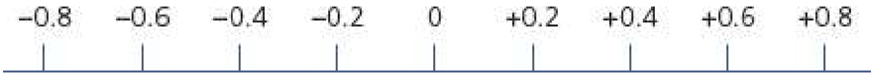

Figure 24.4

In the cell shown in Figure 24.3, the oxidation potential of the zinc anode is +0.76 V, and the reduction potential of the copper cathode is +0.34 V.

$$E_{\text{cell}} = 0.76 + 0.34 = 1.10\ \text{V}$$

Care must be taken to change the signs given in electrode potential data tables to reflect what is happening. These data are given in terms of the *reduction* of the ions concerned. When you are drawing a cell, remember to show the reactants with reduction occurring on the right and oxidation on the left. This means that in the cell described in Figure 24.3 you would write:

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

because zinc atoms are oxidised and copper ions are reduced.

NOW TEST YOURSELF

2 Use the standard electrode potentials in Table 24.1 to calculate the cell potentials for the following electrode pairs:

- **a** $\text{Zn(s)}|\text{Zn}^{2+}\text{(aq)} \parallel \text{Ag}^{+}\text{(aq)}|\text{Ag(s)}$
- **b** $\text{Mg(s)}|\text{Mg}^{2+}\text{(aq)} \parallel \text{Pb}^{2+}\text{(aq)}|\text{Pb(s)}$
- **c** $\text{Cu(s)}|\text{Cu}^{2+}\text{(aq)} \parallel \text{Ag}^{+}\text{(aq)}|\text{Ag(s)}$

Table 24.1

Electrode reaction	Standard electrode potential / V
$\text{Ag}^{+} + \text{e}^{-} \rightleftharpoons \text{Ag}$	+0.80
$\text{Cu}^{2+} + 2\text{e}^{-} \rightleftharpoons \text{Cu}$	+0.34
$\text{Mg}^{2+} + 2\text{e}^{-} \rightleftharpoons \text{Mg}$	−2.38
$\text{Pb}^{2+} + 2\text{e}^{-} \rightleftharpoons \text{Pb}$	−0.13
$\text{Zn}^{2+} + 2\text{e}^{-} \rightleftharpoons \text{Zn}$	−0.76

Non-metal electrodes

Measuring the standard electrode potential of a non-metal element presents different problems. However, you have already seen one way of overcoming this in the hydrogen electrode. The cell shown in Figure 24.5 shows how two non-metallic elements can form a cell.

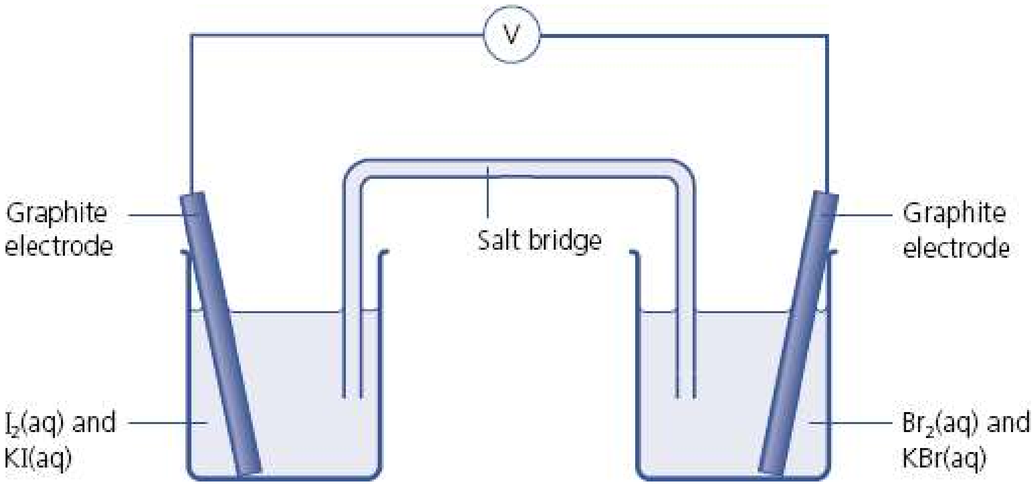

Figure 24.5 A cell formed using two non-metallic elements

The same basic technique can be used for ions of the same element in different oxidation states. The set-up can be seen in Figure 24.6. The electrodes chosen in each case are platinum, although in the laboratory you may have used carbon.

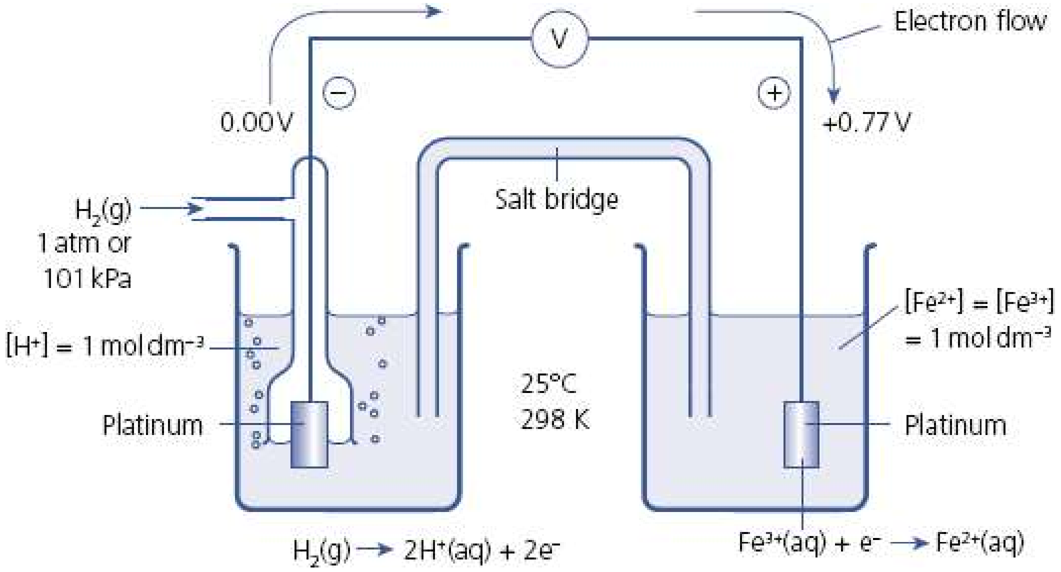

Figure 24.6 A cell formed using ions of the same element

NOW TEST YOURSELF

3 Use the standard electrode potentials in Table 24.2 to calculate the cell potentials for the following electrode pairs, which include non-metals:

- a $Mg(s)|Mg^{2+}(aq) \,||\, ½Cl_2(g)|Cl^-(aq)$
- b $Pb(s)|Pb^{2+}(aq) \,||\, ½Br_2(l)|Br^-(aq)$
- c $Fe^{2+}(aq)|Fe^{3+}(aq) \,||\, ½Cl_2(g)|Cl^-(aq)$
- d $Br^-(aq)|½Br_2(l) \,||\, ½Cl_2(g)|Cl^-(aq)$

Table 24.2

Electrode reaction	Standard electrode potential/V
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	−2.38
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	−0.13

Predicting reactions

As well as using electrode potentials to calculate the voltage that a particular combination of electrodes will produce under standard conditions, they can also be used to predict how likely a given chemical reaction is.

Table 24.3

Metal electrode	Voltage/V	Non-metal electrode	Voltage/V
$K^+ + e^- \rightleftharpoons K$	−2.92	$½F_2 + e^- \rightleftharpoons F^-$	+2.87
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	−2.38	$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52

Metal electrode	**Voltage/V**	**Non-metal electrode**	**Voltage/V**
$Al^{3+} + 3e^- \rightleftharpoons Al$	−1.66	$\frac{1}{2}Cl_2 + e^- \rightleftharpoons Cl^-$	+1.36
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.76	$NO_3^- + 2H^+ + e^- \rightleftharpoons NO_2 + H_2O$	+0.81

In Table 24.3, the half-reactions with high *negative* $E^\ominus$ values do *not* happen readily (think of the reactions of the Group 1 metals with water). By contrast, those with high *positive* $E^\ominus$ values happen spontaneously (think of manganate(VII) as an oxidising agent).

Half-equations can be used to construct full equations by making sure that the numbers of electrons balance and that the overall cell potential is positive. There are some key points that help you to get this right:

- Write the half-equation with the more negative $E^\ominus$ value first.
- Remember that the more positive $E^\ominus$ value will involve a reduction.
- Draw anticlockwise arrows to help predict the overall reaction.

For example, consider the reaction between Fe^{2+} ions and chlorine gas. The two half-equations are shown in Figure 24.7.

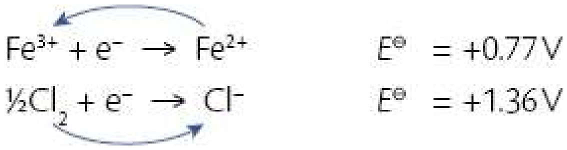

Figure 24.7

Reversing the first equation and adding gives:

$$Fe^{2+} + \tfrac{1}{2}Cl_2 \rightarrow Fe^{3+} + Cl^- \qquad E^\ominus_{cell} = +0.59\,V$$

$E^\ominus_{cell}$ is positive so chlorine gas will oxidise iron(II) ions to iron(III) ions, and be reduced to chloride ions.

The effects of non-standard conditions

For most of the work you will do with electrode potentials, you can assume that conditions are standard, but you do need to know the effects of changing the concentration of an aqueous ion solution.

Think of the half-cell reaction:

$M^{n+}(aq) + ne^- \rightleftharpoons M$

- Le Chatelier's principle (Chapter 7) predicts that, if the concentration of $M^{n+}(aq)$ is increased, then the equilibrium will move to the right.
- If this were the case, the electrode would become more positive with respect to the solution.
- Hence, the electrode potential would also become more positive.
- This also means that the half-cell would become a better oxidising agent. Reducing the concentration of $M^{n+}(aq)$ would have the opposite effect.

The Nernst equation

You can quantify this effect using the Nernst equation:

$$E = E^\ominus + \frac{0.059}{z}\log\frac{[\text{oxidised species}]}{[\text{reduced species}]}$$

where z is the number of electrons transferred in the half-cell reaction, to predict how the value of an electrode potential varies with the concentrations of the aqueous ions.

You can see this by considering the oxidising power of dichromate(VI) ions under different conditions.

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$$

$$E = E^\ominus + \frac{0.059}{6}\log\frac{[Cr_2O_7^{2-}][H^+]^{14}}{[Cr^{3+}]^2}$$

Under standard conditions, $[Cr_2O_7^{2-}(aq)] = [Cr^{3+}(aq)] = [H^+(aq)] = 1.0$ mol dm^{-3}, so E is $E^\ominus$, i.e. 1.33 V.

If you now change the conditions to be in neutral solution, the hydrogen ion concentration is reduced considerably; $[H^+(aq)] = 10^{-7}$ mol dm^{-3}. So with the same concentrations of $Cr_2O_7^{2-}(aq)$ and $Cr^{3+}(aq)$:

$$
\begin{aligned}
E &= 1.33 + \frac{0.059}{6}\log\frac{[1.0][10^{-7}]^{14}}{[1.0]^2} \\
&= 1.33 + 0.00983 \times (\log 1.0 + 14 \log 10^{-7}) \\
&= 1.33 + 0.00983 \times (0 + 14 \times (-7)) \\
&= 1.33 + 0.00983 \times (-98) \\
&= 0.37\,\text{V}
\end{aligned}
$$

Notice that in neutral solution, the dichromate ion has become a relatively weak oxidising agent.

The relationship between $\Delta G^{\ominus}$ and $E^{\ominus}_{\text{cell}}$

The standard electrode potential and the change in Gibbs free energy are linked by the following equation.

$$\Delta G^{\ominus} = -nE^{\ominus}_{\text{cell}}F$$

where n is the number of moles of electrons and F is the Faraday constant. If $E^{\ominus}_{\text{cell}} > 0$, then the process is spontaneous (galvanic cell). If $E^{\ominus}_{\text{cell}} < 0$, then the process is non-spontaneous (electrolytic cell). This is because a positive $E^{\ominus}_{\text{cell}}$ gives a negative value for $\Delta G^{\ominus}$ which, as we saw earlier, means the reaction is spontaneous, and vice versa.

WORKED EXAMPLE

Look at the values of $E^{\ominus}$ for the following half cells.

$\text{Fe} \rightleftharpoons \text{Fe}^{2+} + 2\text{e}^-$ +0.44V [equation 1]

$\text{Fe} \rightleftharpoons \text{Fe}^{3+} + 3\text{e}^-$ +0.04V [equation 2]

$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$ 0.00V [equation 3]

Use the relationship above to show which reaction is the more spontaneous and hence which ion is likely to be formed when metallic iron reacts with dilute acid.

Answer

We are going to use the expression $\Delta G^{\ominus} = -nE^{\ominus}_{cell} F$ to find which reaction has the more negative $\Delta G^{\ominus}$. We can use half-cell values because in both cases the other half-cell is the H_2/H^+ reaction, for which $E^{\ominus}$ is 0.00V.

Remember we have to use E_{cell} = oxidation potential + reduction potential, which is why we have reversed the half-equations for iron.

For equation 1: $\Delta G^{\ominus} = -2 \times 0.44 \times 96\,500 = -84.9$ kJ mol^{-1}

For equation 2: $\Delta G^{\ominus} = -3 \times 0.04 \times 96\,500 = -11.6$ kJ mol^{-1} (both to 3 s.f.)

Equation 1 gives us the more negative value for $\Delta G^{\ominus}$ so that is the more spontaneous reaction.

REVISION ACTIVITY

a Use the standard electrode potentials in Tables 24.2 and 24.3 and the Nernst equation to predict E_{cell} for a cell containing a standard $Fe^{3+}|Fe^{2+}$ electrode and a $Cu|Cu^{2+}$ electrode in which $[Cu^{2+}(aq)]$ is 0.01 mol dm^{-3}.

b How would this cell potential change if a more dilute solution of Cu^{2+} was used?

END OF CHAPTER CHECK

By now you should be able to:

- predict what substances will be liberated during electrolysis from the state of the electrolyte, position in the redox series and concentration
- state and apply the equation $F = Le$
- calculate the quantity of charge passed and the mass/volume of substance liberated during electrolysis
- determine the Avogadro constant by an electrolytic method

- define the terms standard electrode potential $E^\ominus$ and standard cell potential $E^\ominus_{cell}$ and describe the standard hydrogen electrode
- describe methods to measure standard electrode potentials of metals and non-metals and of ions of the same element in different oxidation states
- calculate standard cell potentials using two standard electrode potentials
- use standard cell potentials to deduce the polarity of each electrode, deduce the direction of electron flow and predict the feasibility of a reaction
- deduce the relative reactivity of elements from $E^\ominus$ values and construct redox equations using the relevant half-equations
- predict how the value of the electrode potential varies with the concentration of the aqueous ions both qualitatively and using the Nernst equation
- understand and use $\Delta G^\ominus = -nE^\ominus_{cell} F$