DP IB Chemistry: HL

Your notes

19.1 Electrochemical Cells

Contents

19.1.1 Electrochemical Cells

Your notes

Electrochemical Cells

- We have seen previously that **redox** reactions involve simultaneous **oxidation** and **reduction** as electrons flow from the **reducing agent** to the **oxidizing agent**
- Which way electrons flow depends on the reactivity of the species involved
- Redox chemistry has very important applications in **electrochemical cells**, which come in two types:
 - Voltaic cells
  - Electrolytic cells

Voltaic cells

- A **voltaic cell** generates a potential difference known as an electromotive force or EMF
- The EMF is also called the **cell potential** and given the symbol **E**
- The absolute value of a cell potential cannot be determined only the difference between one cell and another
  - This is analogous to arm-wrestling: you cannot determine the strength of an arm-wrestler unless you compare her to the other competitors

- Voltaic (or Galvanic) cells generate electricity from spontaneous redox reactions
- For example:

$$Zn\,(s) + CuSO_4\,(aq) \rightarrow Cu\,(s) + ZnSO_4\,(aq)$$
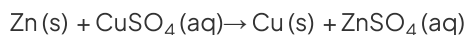
- Instead of electrons being transferred directly from the zinc to the copper ions, a cell is built which separates the two redox processes
- Each part of the cell is called a **half cell**
- If a rod of metal is dipped into a solution of its own ions, an equilibrium is set up
- For example:

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

Your notes
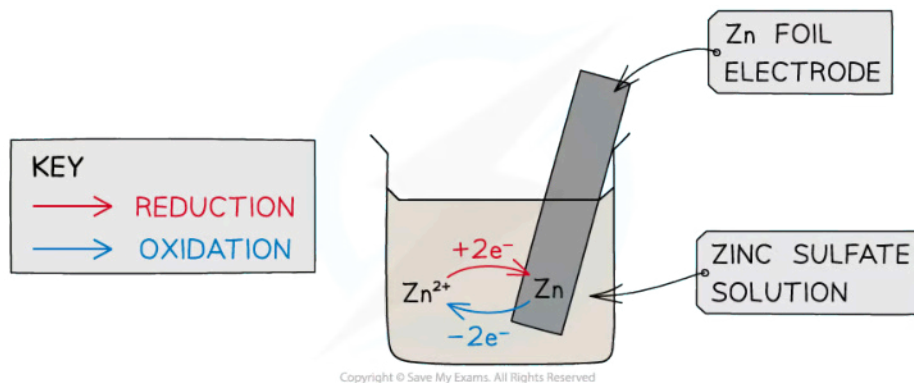
When a metal is dipped into a solution contains its ions an equilibrium is established between the metal and it ions

- This is a **half cell** and the strip of metal is an **electrode**
- The position of the equilibrium determines the **potential difference** between the metal strip and the solution of metal
- The Zn atoms on the rod can deposit two electrons on the rod and move into solution as Zn^{2+} ions:

$$Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$$
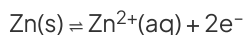
  - This process would result in an accumulation of negative charge on the zinc rod

- Alternatively, the Zn^{2+} ions in solution could accept two electrons from the rod and move onto the rod to become Zn atoms:

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$$
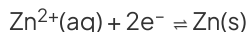
  - This process would result in an accumulation of positive charge on the zinc rod

- In both cases, a potential difference is set up between the rod and the solution
  - This is known as an electrode potential

- A similar electrode potential is set up if a copper rod is immersed in a solution containing copper ions (eg $CuSO_4$), due to the following processes:

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \quad \text{– reduction (rod becomes positive)}$$

$$Cu(s) \rightleftharpoons Cu^{2+}(aq) + 2e^- \quad \text{– oxidation (rod becomes negative)}$$

- Note that a chemical reaction is not taking place – there is simply a potential difference between the rod and the solution

Creating an EMF

Your notes

- If two different electrodes are connected, the potential difference between the two electrodes will cause a current to flow between them. Thus an **electromotive force (EMF)** is established and the system can generate electrical energy
- A typical electrochemical cell can be made by combining a zinc electrode in a solution of zinc sulfate with a copper electrode in a solution of copper sulfate
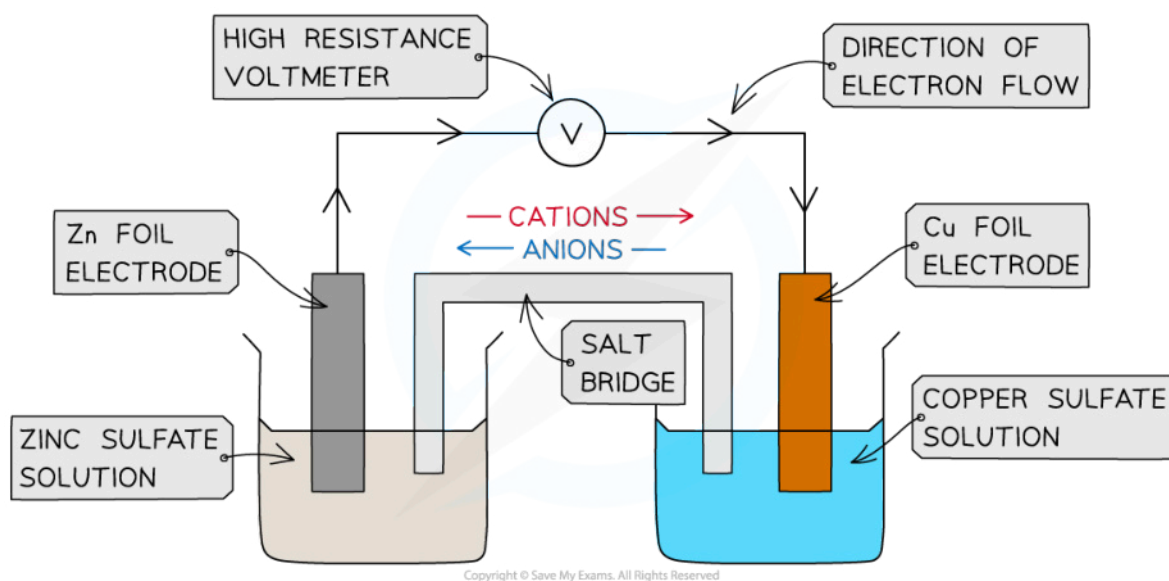
The zinc-copper voltaic cell (also known as the Daniell Cell)

- The circuit must be completed by allowing ions to flow from one solution to the other
- This is achieved by means of a **salt bridge**
    - This is often a piece of filter paper saturated with a solution of an **inert electrolyte** such as $KNO_3(aq)$

- The EMF can be measured using a **voltmeter**
    - Voltmeters have a high resistance so that they do not divert much current from the main circuit

- The two half cells are said to be *in series* as the same current is flowing through both cells
- The combination of two electrodes in this way is known as a voltaic cell, and can be used to generate electricity
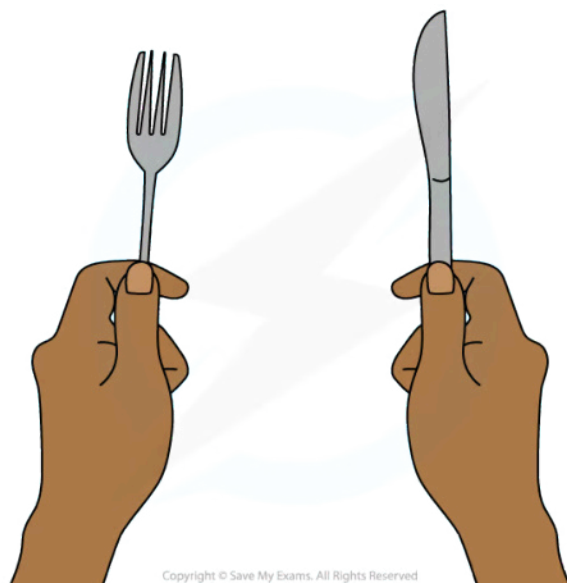
Cell Potential Calculations

- Voltmeters measure potential on the right-hand side of the cell and subtract it from the potential on the left-hand side of the cell

$$\text{EMF} = E_{\text{right}} - E_{\text{left}}$$

- Sometimes this can be hard to remember, but it helps if you remember the phrase 'knives & forks'

You hold your knife in your right hand and your fork in your left hand. EMF is right minus left

- If the standard hydrogen electrode is placed on the left-hand side of the voltmeter, then by convention E_{left} will be zero and the EMF of the cell will be the electrode potential of the right-hand electrode
- For example, if the standard zinc electrode is connected to the standard hydrogen electrode and the standard hydrogen electrode is placed on the left, the voltmeter measures -0.76V.
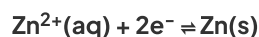
$$\text{Zn}^{2+}\text{(aq)} + 2e^- \rightleftharpoons \text{Zn(s)}$$

- The $\text{Zn}^{2+}\text{(aq)} + 2e^- \rightleftharpoons \text{Zn(s)}$ half-cell thus has an electrode potential of -0.76V

- If the $\text{Cu}^{2+}\text{(aq)} + 2e^- \rightleftharpoons \text{Cu(s)}$ electrode is connected to the standard hydrogen electrode and the standard hydrogen electrode is placed on the left, the voltmeter reads +0.34V
  - The $\text{Cu}^{2+}\text{(aq)} + 2e^- \rightleftharpoons \text{Cu(s)}$ half-cell thus has an electrode potential of +0.34V.

Standard electrode potential

Your notes

- The standard electrode potential of a half-reaction is the emf of a cell where the left-hand electrode is the standard hydrogen electrode and the right-hand electrode is the standard electrode in question
- The equation EMF = E_{RHS} - E_{LHS} can be applied to electrochemical cells in two ways:
  - Calculating an unknown standard electrode potential
  - Calculating a cell EMF

- To be a *standard* electrode potential the measurements must be made at standard conditions, namely:
  - 1.0 mol dm^{-3} ions concentrations
  - 100 kPa pressure
  - 298 K

Calculating an unknown standard electrode potential

- If the RHS and LHS electrode are specified, and the EMF of the cell measured accordingly, then if the E^{θ} of one electrode is known then the other can be deduced.
  - For example, if the standard copper electrode (+0.34 V) is placed on the left, and the standard silver electrode is placed on the right, the EMF of the cell is +0.46 V.
  - Calculate the standard electrode potential at the silver electrode.

$$EMF = E_{RHS} - E_{LHS}$$

$$+0.46 = E^{\theta}{}_{Ag} - (+0.34 \text{ V})$$

$$E^{\theta}{}_{Ag} = 0.46 + 0.34 = +0.80 \text{ V}$$

Calculating a cell EMF

- If both SEP's are known, the EMF of the cell formed can be calculated if the right-hand electrode and left-hand electrode are specified
  - For example, if in a cell the RHS = silver electrode (+0.80V) and LHS is copper electrode (+0.34 V), then

$$EMF = E_{RHS} - E_{LHS}$$

$$EMF = +0.80 - 0.34 = +0.46 \text{ V}$$

Conventional Representation of Cells

- As it is cumbersome and time-consuming to draw out every electrochemical cell in full, a system of notation is used which describes the cell in full, but does not require it to be drawn.
- An electrochemical cell can be represented in a shorthand way by a **cell diagram** (sometimes called cell representations or cell notations)
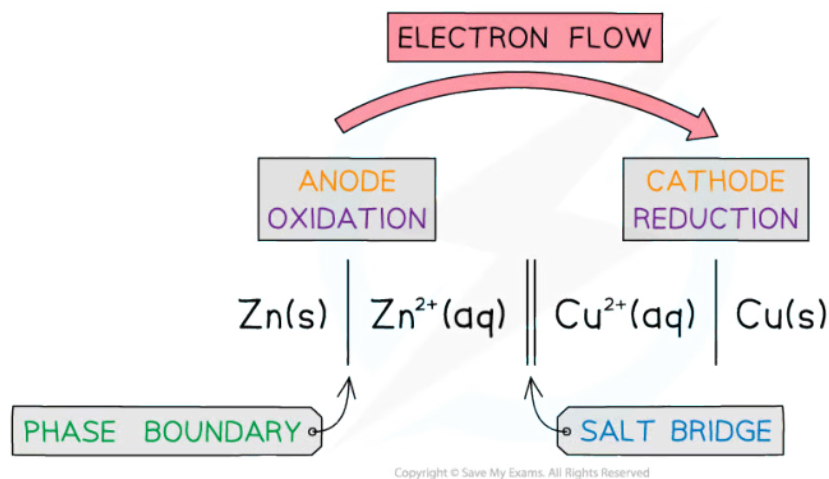
The conventional representation of voltaic cells

- By convention, the half cell with the greatest negative potential is written on the left of the salt bridge, so $E^\theta_{cell} = E^\theta_{right} - E^\theta_{left}$
  - In this case, $E^\theta_{cell} = +0.34 - -0.76 = +1.10$ V.

- The left cell is being oxidized while the right is being reduced
- If there is more than one species in solution, and the species are on different sides of the half-equation, the different species are separated by a comma
- This method of representing electrochemical cells is known as the conventional representation of a cell, and it is widely used
- If both species in a half reaction are aqueous then an inert platinum electrode is needed which is recorded on the outside of the half cell diagram

Some Examples

- For the iron(II) and iron(III) half cell reaction a platinum electrode is needed as an electron carrier
- The half equation is

$$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$$
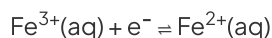
- So the cell convention as a left hand electrode would be

$$Pt \equiv Fe^{2+}(aq), Fe^{3+}(aq)$$
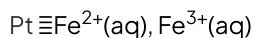
- Notice the order must be Fe(II) then Fe(III) as the left side is an oxidation reaction, so Fe(II) is oxidised to Fe(III) by the loss of an electron
- The platinum electrode is separated by the phase boundary (vertical solid line), but the iron(II) and iron(III) are separated by a comma since they are in the same phase
- Non-metals will also require a platinum electrode
- If chlorine is used as an electrode the reduction reaction is

$$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$$
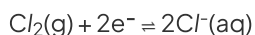
- The conventional representation of the half reaction would be

$$Cl_2(g), 2Cl^-(aq) \,|\, Pt$$
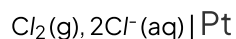
- Notice that the half cell reaction is balanced; however, it would be also correct to write it as

$$Cl_2(g), Cl^-(aq) \,|\, Pt$$
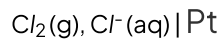
- This is because conventional cell diagrams are not quantitative- they are just representations of the materials and redox processes going on
  - Most chemists tend to show them balanced anyway

- Combining these two half cells together gives

$$Pt \,|\, Fe^{2+}(aq), Fe^{3+}(aq) \,\|\, Cl_2(g), 2Cl^-(aq) \,|\, Pt$$
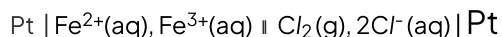
- As you can see the overall cell diagram is not quantitative as the left side is a one electron transfer and the right side is a two electron transfer
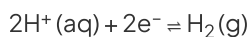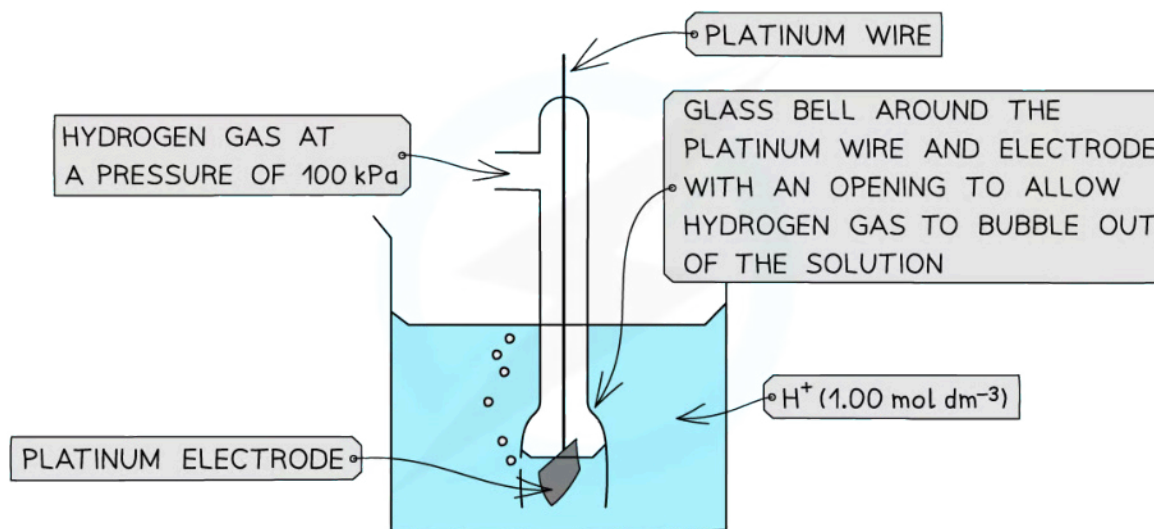
19.1.2 The Standard Hydrogen Electrode

The Standard Hydrogen Electrode

- The absolute value of a half cell potential cannot be measured, only differences in potential between pairs of half-cells.
- For this reason, it is necessary to have a standard electrode against which all other half-cells can be compared
- The **standard hydrogen electrode** is a half-cell used as a **reference electrode** and consists of:
  - Hydrogen gas in equilibrium with H^+ ions of concentration 1.00 mol dm^{-3} (at 100 kPa)

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

  - An **inert platinum** electrode that is in contact with the hydrogen gas and H^+ ions
- It is given an arbitrary value of E^θ = 0.00 volts
- When the standard hydrogen electrode is connected to another half-cell, the **standard electrode potential** of that half-cell can be read from a high resistance voltmeter

The standard electrode potential of a half-cell can be determined by connecting it to a standard hydrogen electrode

- In fact, the hydrogen electrode is rarely used in practice for a number of reasons:
  - The electrode reaction is slow
  - The electrodes are not easily portable
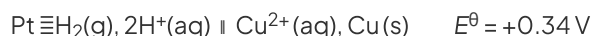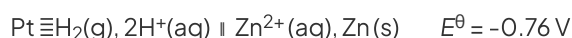 - It is difficult to maintain a constant pressure

- Once one standard electrode potential has been measured relative to the standard hydrogen electrode, it is not necessary to use the standard hydrogen electrode again
- Any electrode whose electrode potential is known could be used to measure standard electrode potentials

Measurements using the hydrogen electrode

- If a hydrogen electrode is used to measure the electrode potentials of zinc and copper half reactions, the conventional cell diagrams would be:

$$Pt \equiv H_2(g), 2H^+(aq) \parallel Zn^{2+}(aq), Zn(s) \qquad E^\theta = -0.76 \text{ V}$$

$$Pt \equiv H_2(g), 2H^+(aq) \parallel Cu^{2+}(aq), Cu(s) \qquad E^\theta = +0.34 \text{ V}$$

- Since the hydrogen electrode is always on the left, the polarity of the half cell measured is always with respect to hydrogen
- The half reaction will therefore always be a reduction reaction, so that is why sometimes standard electrode potentials are termed **standard reduction potentials**
- Tables of standard electrode potentials have been compiled ranking half cells from negative to positive values

Table of standard electrode potentials

Oxidised species $\rightleftharpoons$ Reduced species	E^θ (V)
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.04
$K^+(aq) + e^- \rightleftharpoons K(s)$	−2.93
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	−2.87
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.37

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- The more negative the value; the better the half cell is at pushing electrons so the equilibrium lies to the left
- This means the more negative the half cell; the better it can act as a reducing agent

Your notes

💡 Examiner Tip

You might find this a helpful mnemonic for remembering the redox processes in cells

Lio the lion goes Roor!

Lio stands for 'Left Is Oxidation' and he is saying ROOR because that is the order of species in the cell diagram:

Reduced $\equiv$ Oxidised ‖ Oxidised$\equiv$Reduced

Pt $\equiv$Fe^{2+}(aq), Fe^{3+}(aq) ‖ Cl$_2$ (g), 2Cl$^-$ (aq) $\equiv$Pt

19.1.3 Electrolysis of Aqueous Solutions

## Electrolysis of Aqueous Solutions

- We have seen previously how simple binary compounds can be electrolysed when molten and the products of electrolysis can be predicted using our knowledge of the ions present
- At the cathode, positive metals ions (cations) are discharged resulting in metals being deposited
- The cations are reduced by the electrons coming from the cathode:

$$Pb^{2+}(l) + 2e^- \rightarrow Pb\ (l)$$
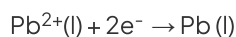
- Meanwhile, at the anode, anions are discharged by oxidation:

$$2Br^-\ (l) \rightarrow Br_2\ (g) + 2e^-$$

- However, when aqueous solutions of ionic compounds are electrolysed the products are a little more complicated to predict as there are additional ions present from the water
- Water can be oxidised to oxygen or reduced to hydrogen:
    - Oxidation reaction:

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

    - Reduction reaction:

$$2H_2O\ (l) + 2e^- \rightarrow H_2\ (g) + 2OH^-\ (aq)$$
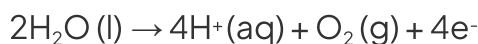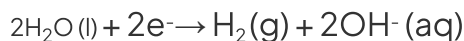
- At the cathode, either the metal ion M^+ or water can be reduced
- At the anode, either the anion A^- or water can be oxidized
- Which species is discharged depends on three things:
    - The **relative values of** E^θ
    - The **concentration** of the ions present
    - The **identity** of the electrode

Products of specified electrolytes

- The electrolysis of water, sodium chloride solution and copper sulfate solutions is as follows:

Table showing the electrolysis products of aqueous solutions
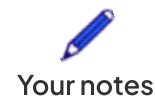
Substance used	Cathode product	Anode product
Water	hydrogen	oxygen
Sodium chloride	hydrogen	oxygen/chlorine
Copper sulphate solution with inert electrodes	copper	oxygen
Copper sulphate solution with copper electrodes	copper	–

The influence of relative values of E^θ

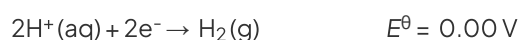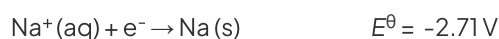- The electrolysis of water is very slow as there are few ions present, so a little acid or base can be added to increase the number of ions present and speed up the electrolysis
- Whether acid or base is added the products are the same, but the electrode reactions are slightly different
- Using dilute sulfuric acid as the electrolyte, the cathode reactions could be

$$2H_2O\,(l) + 2e^- \rightarrow H_2\,(g) + 2OH^-\,(aq) \qquad E^\theta = -0.83V$$

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

- The E^θ is smaller for the hydrogen ion so it is preferentially reduced and H_2 (g) will be discharged
- At the anode, although sulfate ions are present in the solution, only water can be oxidised
- This is because the sulfate ion, $SO_4{}^{2-}$, contains sulfur in its maximum oxidation state (+6) so it cannot be further oxidised
- The oxidation of water produces oxygen gas:

$$2H_2O\,(l) \rightarrow 4H^+\,(aq) + O_2\,(g) + 4e^- \qquad E^\theta = -1.23\,V$$
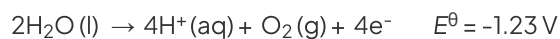
- If the water is made basic by the addition of dilute sodium hydroxide solution, the cathode reactions could be:

$$Na^+\,(aq) + e^- \rightarrow Na\,(s) \qquad E^\theta = -2.71\,V$$

$$2H_2O\,(l) + 2e^- \rightarrow H_2\,(g) + 2OH^-\,(aq) \qquad E^\theta = -0.83\,V$$

- The E^θ is smaller for water than the sodium ion, so water is preferentially reduced and H_2 (g) will be discharged
- At the anode, either the hydroxide ion or water can be oxidised:

$$4OH^- (aq) \rightarrow 2H_2O (l) + O_2 (g) + 4e^- \qquad E^\theta = -0.40 \text{ V}$$

$$2H_2O (l) \rightarrow 4H^+ (aq) + O_2 (g) + 4e^- \qquad E^\theta = -1.23 \text{ V}$$
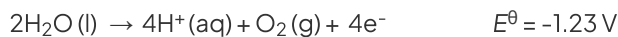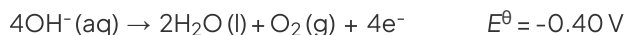
- Based on these values the hydroxide ion is preferentially oxidized and O_2 (g) will be discharged
- The overall reaction whether in acid or alkali conditions is:

$$2H_2O (l) \rightarrow 2H_2 (g) + O_2 (g)$$
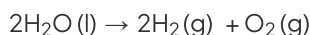
The influence of concentration of the ions

- The electrolysis of sodium chloride solution provides an illustration of the influence of concentration on the products discharged
- As before, we would expect hydrogen ion to be preferentially discharged at the cathode before the sodium ion:

$$2H^+ (aq) + 2e^- \rightarrow H_2 (g) \qquad E^\theta = 0.00 \text{ V}$$

- However at the anode, the relative proximity of the E^θ values allows the possibility of both reactions occurring:

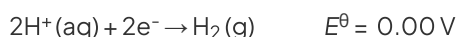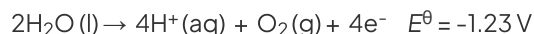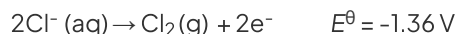$$2Cl^- (aq) \rightarrow Cl_2 (g) + 2e^- \qquad E^\theta = -1.36 \text{ V}$$

$$2H_2O (l) \rightarrow 4H^+ (aq) + O_2 (g) + 4e^- \quad E^\theta = -1.23 \text{ V}$$

- In fact, when concentration of the sodium chloride increases to more than 25% the Cl^- becomes preferentially discharged and chlorine gas is the main product of the reaction at the anode
- The overall reaction equation is:

$$2NaCl (aq) + 2H_2O (l) \rightarrow 2NaOH (aq) + H_2 (g) + Cl_2 (g)$$

Influence of the electrodes

- The products of electrolysis are influenced by the identity of the electrodes
- Electrodes that take part in the redox processes are known as **active electrodes** and inert electrodes such as platinum and carbon are called **passive electrodes**
- The electrolysis of copper sulfate solution, $CuSO_4$ (aq), is an example of where active and passive electrodes determine the products

Passive electrodes

- At the cathode, the possible reactions that could take place are:

$$Cu^{2+} (aq) + 2e^- \rightarrow Cu (s) \qquad E^\theta = +0.34 \text{ V}$$

$$2H_2O (l) + 2e^- \rightarrow H_2 (g) + 4OH^- (aq) \qquad E^\theta = -0.83 \text{ V}$$
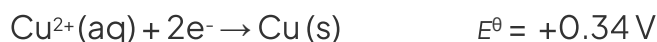
- Copper ions are preferentially reduced, so copper metal is deposited on the cathode

- At the anode, water is oxidised, so oxygen gas is produced (the sulfate ion cannot be oxidised):

$$2H_2O\,(l) \rightarrow 4H^+\,(aq) + O_2\,(g) + 4e^- \quad E^\theta = -1.23\,V$$
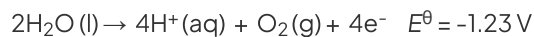
- The overall equation for the reaction is:

$$2CuSO_4\,(aq) + 2H_2O\,(l) \rightarrow 2Cu\,(s) + O_2\,(g) + 2SO_4^{2-}\,(aq) + 4H^+\,(aq)$$

OR

$$2CuSO_4\,(aq) + 2H_2O\,(l) \rightarrow 2Cu\,(s) + O_2\,(g) + 2H_2SO_4\,(aq)$$
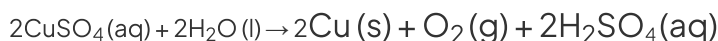
Active electrodes

- At the cathode, the reaction is the same as with inert electrodes:

$$Cu^{2+}\,(aq) + 2e^- \rightarrow Cu\,(s) \qquad E^\theta = +0.34\,V$$
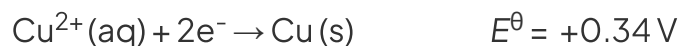
- However, at the anode, the copper electrode is oxidised and dissolves to form copper ions

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

- This reaction is used to purify copper, needed to produce a very high grade of copper for use in electrical wires
- The anode is made of impure copper and the cathode is made of pure copper
- The impurities from the anode fall to the bottom of the cell

Your notes

ANODE MADE OF IMPURE COPPER

CATHODE MADE OF PURE COPPER

ANODE SLIME CONTAINING IMPURITIES & PRECIOUS METALS

COPPER SULFATE SOLUTION

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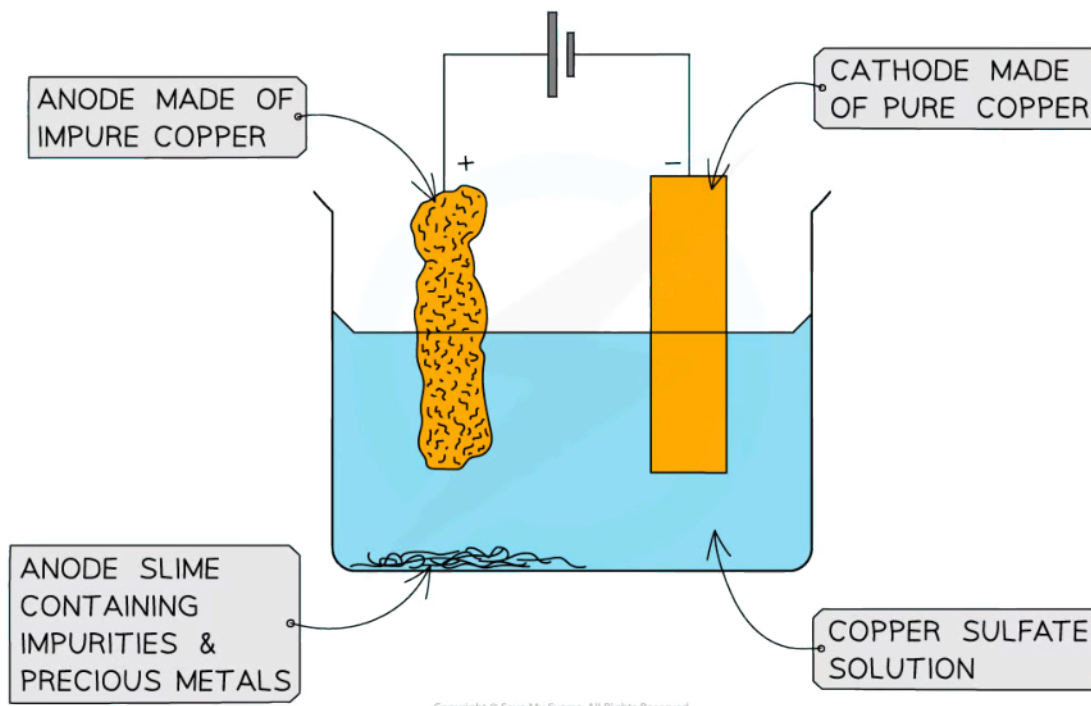
The purification of copper by electrolysis

- The anode slowly dissolves away and the cathode builds up pure copper
- The impurities form a slime under the anode which is actually quite valuable as it often contains significant quantities of precious metals like silver

19.1.4 Quantitative Electrolysis

Quantitative Electrolysis

- Michael Faraday showed, in 1833, that the amount of products obtained is dependent on the quantity of electrical charge passed through the cell
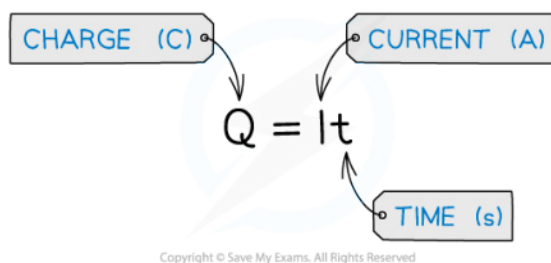- Electrical charge is a measure of the current passed and the time taken, and they are related in the following way:

The formula for calculating charge

- The SI unit of electric current (symbol **I**) is the **ampere**, usually known as the **amp (A).**
- The SI unit of electric charge (symbol **Q**) is the **coulomb (C)**
  - It is the amount of charge transported in 1 second by a current of 1 ampere

- The equation above can be written as:

Coulombs = Amps x seconds

C = A x s

- The charge on a single electron is 1.602×10^{-19} C, so one mole of electrons carries a charge of:

$$1.602 \times 10^{-19} \, C \times L = 1.602 \times 10^{-19} \times 6.02 \times 10^{23} = 96\,440.4 \, C\,mol^{-1}$$

- This quantity is known as **Faraday's constant** or just the **Faraday** and is given the symbol F
- At this level for the purposes of calculations, this figure is rounded to **96 500 C mol^{-1}**
- To calculate the mass of a product at an electrode, knowing the current and time we follow these steps:

1	CALCULATE THE CHARGE PASSED, Q

$Q = It$
$C = A \times s$

2	CALCULATE THE NUMBER OF FARADAYS, F

$F = \dfrac{Q}{96\,500}$

3	DEDUCE THE AMOUNT OF PRODUCT IN MOLES, n, USING THE EQUATION

n

4	FIND THE MASS OF PRODUCT, m, USING THE MOLAR MASS, M

$m = n \times M$
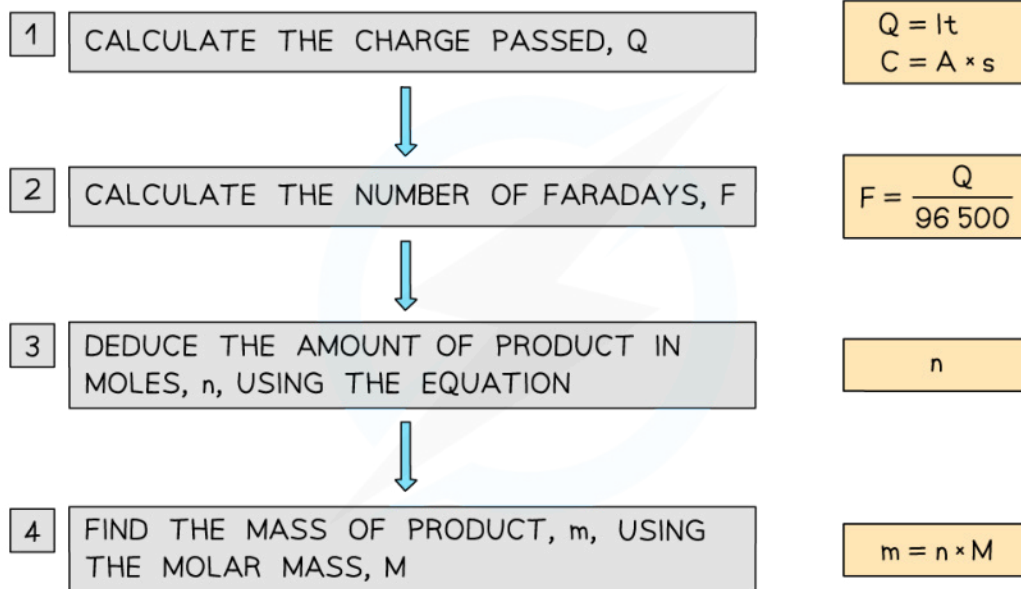
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Solving problems in quantitative electrolysis

✏️ Worked example

What mass of nickel is formed if a solution of nickel(II) sulfate is electrolysed for 10.0 mins using a current of 2.50 A?

Answer

- The amount of charge passed is:

$$Q = 2.50 \times 10 \times 60 = 1500\ C$$

- The number of Faradays is:

$$F = 1500 \div 96\,500 = 0.01554\ mol$$

- The half equation is:

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

- The mole ratio shows 2 moles electrons = 1 mole of Ni
- So, the amount of nickel is

$$n = 0.01554\ mol \div 2 = 0.00777\ mol$$

- The mass of nickel is

$$m = n \times M = 0.00777 \text{ mol} \times 58.69 \text{ g mol}^{-1} = \textbf{0.456 g}$$

Your notes

Relative amounts of products in electrolysis

- The half equations in electrolysis can be used to deduce the relative amounts of products at each electrode
- By looking at the amount of electrons needed to balance the half equations, we can deduce how much, in moles, of different products can be obtained by the same amount of charge passed
- Comparing the electrolysis of molten potassium chloride and lead chloride, the cathode reactions are:

$$K^+(l) \quad + \quad e^- \quad \rightarrow \quad K(l)$$

1 mole of electrons   1 mole of potassium

$$Pb^{2+}(l) \quad + \quad 2e^- \quad \rightarrow \quad Pb(s)$$
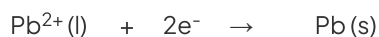
2 moles of electrons   1 mole of lead

- We can see that twice as many moles of electrons are needed to produce 1 mole of lead compared to 1 mole of potassium
- Alternatively, we can say that the same quantity of charge produces half as much lead as potassium (in moles)

🖊️ **Worked example**

A solution of silver nitrate, $AgNO_3$, is electrolysed for 20 mins at a current of 1.50 A.1) How much silver, in moles, is formed at the cathode?2) How much copper, in moles, would be produced if the same reaction was carried out using copper(II) sulfate solution in place of silver nitrate?

Answer

Answer 1:

- The amount of charge passed is:

$$Q = 1.50 \times 20 \times 60 = 1800 \text{ C}$$

- The number of Faradays is

$$F = 1800 \div 96\,500 = 0.01865 \text{ mol}$$

- The charge on the silver ion is +1, so **0.01865 mol** of silver are produced

Answer 2:

- The half equations for silver and copper(II) are:

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

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$
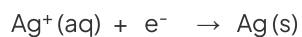
- The same quantity of electrical charge will produce 2Ag : 1Cu
- The amount of copper would be 0.01865 mol ÷ 2 = **0.009325 mol**

> 💡 **Examiner Tip**
>
> There is no need to learn the value of Faraday's constant as it is given in Section 2 of the Data booklet.

19.1.5 Free Energy & E°

Free Energy & E°

- Previously we have seen the concept and term **free energy,** ΔG^θ
- Free energy is a measure of the available energy to do useful work and takes into account the entropy change, ΔS^θ, as well as the enthalpy change of a reaction, ΔH^θ
- For reactions to be **spontaneous**, the free energy change must be negative
- We have also seen that to calculate a cell potential using standard electrode potentials we use the expression:

$$\text{EMF} = E_{RHS} - E_{LHS}$$

- This is not an arbitrary arrangement of the terms
- The convention of placing the half cell with the greatest negative potential on the left of the cell diagram ensures that you will always get a positive reading on the voltmeter, corresponding to the spontaneous reaction
  - If you have done an experiment on measuring electrode potentials, you have probably been told to 'swap the terminals if you don't get a positive reading on the voltmeter'

- In electrochemical cells, a spontaneous reaction occurs when the combination of half cells produces a positive voltage through the voltmeter, i.e. the more negative electrode pushes electrons onto the more positive electrode
- It doesn't really matter if you are using a digital multimeter as a voltmeter as you will still get a reading (with the wrong sign), but analogue voltmeters will only work if the terminals are correctly connected to the positive and negative half cells
- This should give you an insight into why the following statements are true:

If ΔE^θ is positive, the reaction is spontaneous as written

If ΔE^θ is negative, the forward reaction is non-spontaneous but the reverse reaction will be spontaneous

- You should now be able to see that there is a link between ΔG^θ and E^θ
- This relationship is the equation:

$$\Delta G^\theta = -nFE^\theta$$

where:

- n= number of electrons transferred
- F= the Faraday constant, $96\,500\ \text{C mol}^{-1}$

- When a reaction has reached equilibrium, there is no free energy change so ΔG^θ is zero and it follows that E^θ must also be zero
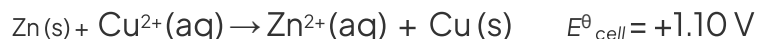
- This is effectively what happens when the reactants in a voltaic cell have been exhausted and there is no longer any push of electrons from one half cell to the other

---

✏️ Worked example

The spontaneous reaction between zinc and copper in a voltaic cell is shown below

$$Zn\,(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu\,(s) \qquad E^{\theta}{}_{cell} = +1.10\ V$$

Calculate the free energy change, ΔG^{θ}, for the reaction.

Answer

- Write the equation:

$$\Delta G^{\theta} = -nFE^{\theta}$$

- Substitute the values

$$\Delta G^{\theta} = -2 \times 96\,500\ C\ mol^{-1} \times 1.10\ V = -212300\ C\ mol^{-1}V$$

- This looks a strange unit. However, by definition 1J = 1V x 1C, so this answer can be expressed as

$$\Delta G^{\theta} = -212300\ J\ mol^{-1} \text{ or } -212.3\ kJ\ mol^{-1}$$

- The three conditions of free energy and electrode potential are summarised below

Summary table of the conditions of free energy and electrode potential

Free energy change	Standard electrode potential	Reaction
$\Delta G^{\theta} = -ve$	$E^{\theta}_{cell} = +ve$	The reaction is spontaneous
$\Delta G^{\theta} = +ve$	$E^{\theta}_{cell} = -ve$	The reaction is non-spontaneous
$\Delta G^{\theta} = 0$	$E^{\theta}_{cell} = 0$	The reaction is at equilibrium

> ### 💡 Examiner Tip
>
> The equation $\Delta G^\theta = -nFE^\theta$ is given in Section 1 of the Data Book so there is no need to memorise it

Your notes

Predicting Spontaneous Reactions

- To predict the spontaneous reaction, we simply need to find the relevant half equations and electrode potentials
- From this information, we can deduce the spontaneous and non-spontaneous reaction
- By using the convention:

$$\text{EMF} = E_{\text{RHS}} - E_{\text{LHS}}$$

- A positive EMF is obtained from the spontaneous reaction which occurs when the most negative half cell is E_{LHS} and the most positive is E_{RHS}
- The left side is always where oxidation takes place so we can also us an alternative form of the relationship:

$$\text{EMF} = E_{\text{reduction}} - E_{\text{oxidation}}$$

> ### ✏️ Worked example
>
> Using data from Table 24 of the Data Book, determine if the reaction shown is spontaneous at standard conditions
>
> $$\text{Sn (s)} + \text{Mn}^{2+} \text{(aq)} \rightarrow \text{Sn}^{2+} \text{(aq)} + \text{Mn (s)}$$
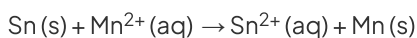
Answer

- Table 24 of the Data Book shows the following half reactions

$$\text{Sn}^{2+} \text{(aq)} + 2e^- \rightarrow \text{Sn (s)} \qquad E^{\theta} = -0.14 \text{ V}$$

$$\text{Mn}^{2+} \text{(aq)} + 2e^- \rightarrow \text{Mn (s)} \qquad E^{\theta} = -1.18 \text{ V}$$
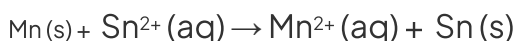
- Manganese is the more negative value, so will be E_{LHS} or $E_{\text{oxidation}}$ in the spontaneous reaction

$$\text{EMF} = E_{\text{RHS}} - E_{\text{LHS}} = (-0.14) - (-1.18) = +1.04$$

- For oxidation to take place, the manganese must lose electrons and the tin(II) must gain electrons

$$\text{Mn (s)} \rightarrow \text{Mn}^{2+} \text{(aq)} + 2e^- \text{ and } \text{Sn}^{2+} \text{(aq)} + 2e^- \rightarrow \text{Sn (s)}$$

- So, the spontaneous reaction is

$$\text{Mn (s)} + \text{Sn}^{2+} \text{(aq)} \rightarrow \text{Mn}^{2+} \text{(aq)} + \text{Sn (s)}$$

- Therefore, the reaction in the question is **not** spontaneous

> 💡 **Examiner Tip**
>
> **A word of caution**Although the positive E^θ indicates a reaction should take place, you might not actually see anything taking place if you constructed a cell that is predicted to be spontaneous. This is because like free energy changes, E^θ only predicts the energetic feasibility for a reaction and it does not take into account the rate of a reaction. A reaction could have a really high activation energy making it impossibly slow at room temperature.
>
> 'THERMODYNAMICS PREDICTS; KINETICS CONTROLS'

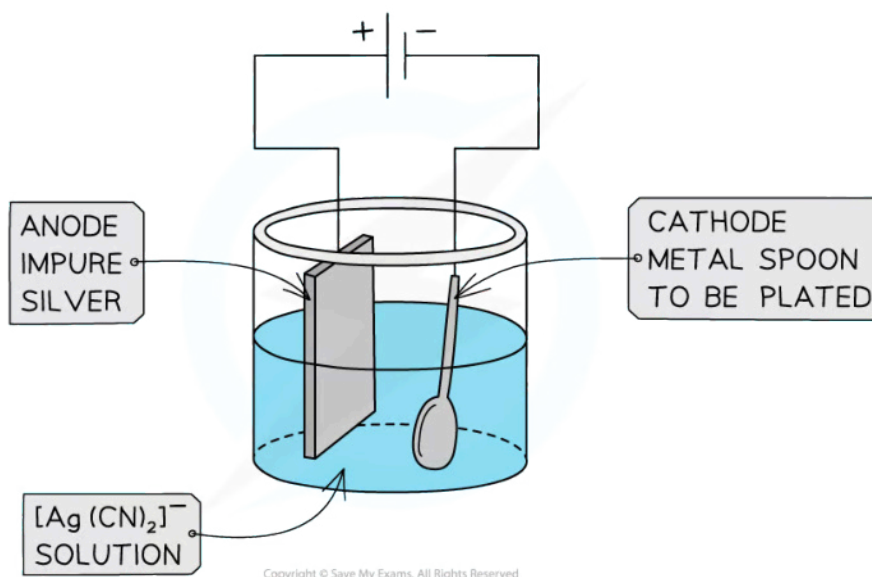## 19.1.6 Electroplating

Your notes

Electroplating

- As we have seen, electrolysis with active electrodes involves the deposit of metals onto the surface of the cathode
- Electroplating involves the electrolytic coating of an object with a very thin metallic layer
- This is done for the purposes of decoration or for corrosion prevention
- For example, gold plated jewellery is made for aesthetic reasons and iron is galvanized with zinc to protect the iron from rusting
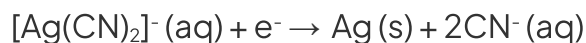

Electroplating an object with silver

- For successful electroplating, the metal needs to be deposited slowly and evenly
- The anode is usually made from the same metal to replenish the loss of the metal during electrolysis and maintain a constant concentration of the electrolyte
- Sodium silver cyanide, $Na[Ag(CN)_2]$, also know as sodium dicyanoargentate(I), is the preferred electrolyte for silver plating
- The reaction at the anode is:

$$Ag\,(s) + 2CN^-\,(aq) \rightarrow [Ag(CN)_2]^-\,(aq) + e^-$$
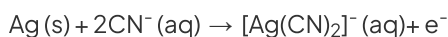
- The reaction at the cathode is:

$$[Ag(CN)_2]^-\,(aq) + e^- \rightarrow Ag\,(s) + 2CN^-\,(aq)$$

- Impure silver is made the anode and it slowly dissolves away during the electrolysis

- By controlling the current, time and concentration of the electrolyte the rate of deposition can be carefully controlled to adjust the thickness of the metallic layer
- Even plastics have been electroplated using an ingenious process where the surface of the plastic is pitted and then imbedded with metallic particles that conduct electricity and can then be metal plated

Your notes