HL IB Chemistry

Electron Transfer Reactions

Contents

Oxidation & Reduction

Oxidation & Reduction

Oxidising agent

- An **oxidising agent** is a substance that **oxidises** another atom or ion by causing it to lose electrons
- An oxidising agent itself gets **reduced – gains electrons**
- Therefore, the **oxidation number** of the oxidising agent **decreases**

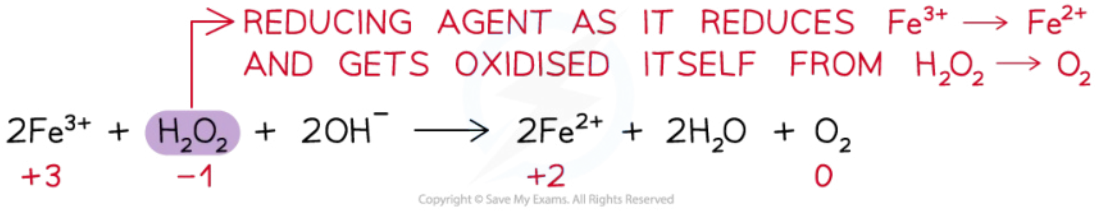
H_2O_2 acting as the oxidising agent

Example of an oxidising agent in a chemical reaction

Reducing agent

- A **reducing agent** is a substance that **reduces** another atom or ion by causing it to gain electrons
- A reducing agent itself gets **oxidised – loses/donates electrons**
- Therefore, the **oxidation number** of the reducing agent **increases**

H_2O_2 acting as a reducing agent



Example of a reducing agent in a chemical reaction

- For a reaction to be recognised as a redox reaction, there must be both an oxidising and reducing agent
- Some substances can act both as oxidising and reducing agents
- Their nature is dependent upon what they are reacting with and the reaction conditions

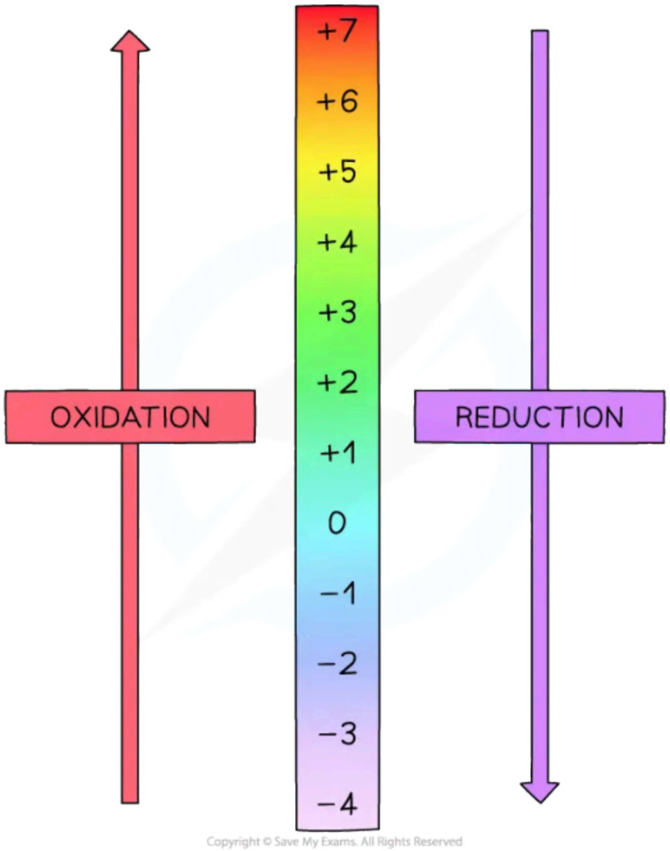
Oxidising & Reducing Agents Table

Oxidising agents....	Reducing agents....

.... oxidise other species	.... reduce other species
.... accept electrons	.... donate electrons
.... are themselves reduced	.... are themselves oxidised

- Applying the definitions of oxidising and reducing agents allows you to identify them in chemical equations
- By deducing the oxidation numbers of the species you can determine whether it has been oxidised or reduced

Oxidation number of redox line



A visual reminder of oxidation numbers and redox. This is like an elevator in a building going up to higher floors is oxidation and going down to the basement is reduction

Worked example

Four reactions are shown. In which reaction is the species in blue acting as an oxidising agent?

A. $Cr_2O_7^{2-} + 8H^+ + 3SO_3^{2-} \rightarrow 2Cr^{3+} + 4H_2O + 3SO_4^{2-}$

B. $Mg + Fe^{2+} \rightarrow Mg^{2+} + Fe$

C. $Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$

D. $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

Answer:

- The correct option is **B**.
  - Oxidising agents are substances that oxidise other species, gain electrons and are themselves reduced.
  - Write down the oxidation numbers of each species in the reaction

$$\begin{array}{ccccccc} 0 & & +2 & & +2 & & 0 \\ \mathbf{Mg} & + & \mathbf{Fe^{2+}} & \rightarrow & \mathbf{Mg^{2+}} & + & \mathbf{Fe} \end{array}$$

  - In equation B, Fe^{2+} oxidises Mg(0) to Mg^{2+}(+2) and is itself reduced from Fe^{2+}(+2) to Fe(0)

Examiner Tip

- Don't forget:
  - Oxidation is the gain of oxygen or the loss of hydrogen
  - Reduction is the loss of oxygen or the gain of hydrogen
- Using these other definitions can make it quicker / easier to spot which species is being reduced or oxidised

Half Equations

Half Equations

How to balance a redox equation

- Oxidation numbers can be used to balance chemical equations
- Go through these steps to balance a redox equation:
  1. **Write the unbalanced equation and identify the atoms which change in ox. no.**
  2. **Deduce the oxidation number changes**
  3. **Balance the oxidation number changes**
  4. **Balance the charges**
  5. **Balance the atoms**

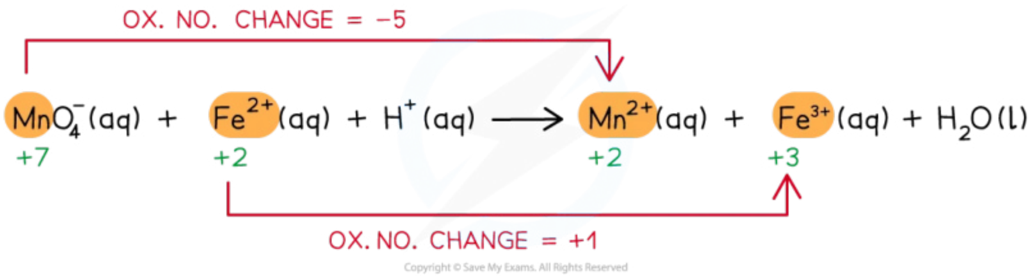
Worked example

Manganate(VII) ions (MnO_4^-) react with Fe^{2+} ions in the presence of acid (H^+) to form Mn^{2+} ions, Fe^{3+} ions and water. Write the overall redox equation for the reaction

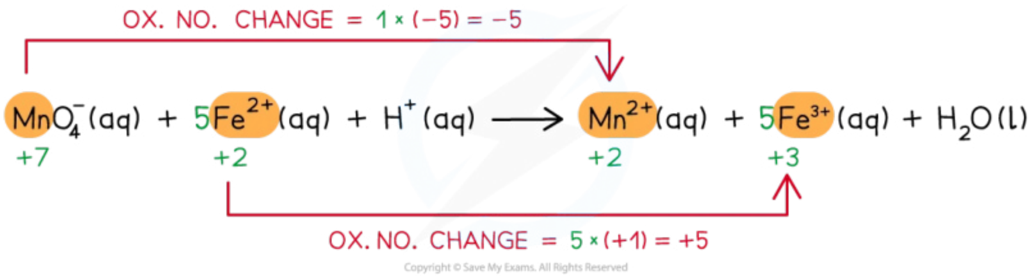
Answer:

1. Write the unbalanced equation and identify the atoms which change in oxidation number

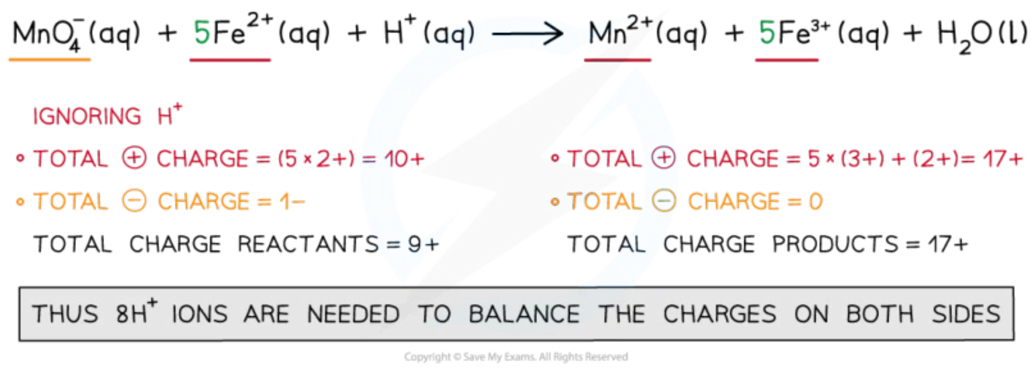
2. Deduce the oxidation number changes



3. Balance the oxidation number changes



4. Balance the charges



5. Balance the atoms
   -

$$MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$

Redox titrations

- In **titrations**, the concentration of a solution is determined by titrating with a solution of known concentration.
- In redox titrations, an **oxidising agent** is titrated against a **reducing agent**
  - Electrons are transferred from one species to the other
- **Indicators** are sometimes used to show the endpoint of the **titration**
- However, most **transition metal ions** naturally change colour when changing **the oxidation state**
- There are two common **redox titrations** you should know about:
  - **Manganate(VII) titrations**
  - **Iodine-thiosulfate titrations**

Manganate(VII) titrations

- A redox reaction occurs between acidified manganate(VII) ions and iron(II) ions:

$$MnO_4^- (aq) + 8H^+ (aq) + 5Fe^{2+} (aq) \rightarrow Mn^{2+} (aq) + 5Fe^{3+} (aq) + 4H_2O (l)$$

- This reaction needs no indicator as the manganate(VII) is a strong purple colour which disappears at the endpoint, so the titration is self-indicating
- This reaction is often used for the analysis of iron for example in iron tablets (health supplements)

Iodine-thiosulfate titrations

- A redox reaction occurs between iodine and thiosulfate ions:

$$2S_2O_3^{2-} (aq) + I_2 (aq) \rightarrow 2I^- (aq) + S_4O_6^{2-} (aq)$$

- The light brown/yellow colour of the iodine turns paler as it is converted to colourless iodide ions
- When the solution is a straw colour, **starch** is added to clarify the endpoint
- The solution turns blue/black until all the iodine reacts, at which point the colour disappears.
- This titration can be used to determine the concentration of an **oxidising agent**, which **oxidises** iodide ions to iodine molecules
- The amount of iodine is determined from **titration** against a known quantity of sodium thiosulfate solution
- This reaction can be used for the analysis of chlorine in bleach

Worked example

A health supplement tablet containing iron(II)sulfate was analysed by titration. A tablet weighing 2.25 g was dissolved in dilute sulfuric acid and titrated against 0.100 mol dm^{-3} $KMnO_4$.The titration required 26.50 cm^3 for a complete reaction. Calculate the percentage by mass of iron in the table.

Answer:

1. Write the balanced equation for the reaction
    - oxidation: Fe^{2+} (aq) → Fe^{3+} (aq) + e^-
    - reduction: MnO_4^- (aq) + $8H^+$ (aq) + $5e^-$ → Mn^{2+} (aq) + $4H_2O$ (l)
    - overall: **MnO_4^- (aq) + $8H^+$ (aq) + $5Fe^{2+}$ (aq) → Mn^{2+} (aq) + $4H_2O$ (l) + $5Fe^{3+}$ (aq)**

2. Determine the amount of MnO_4^- used in the titration
    - moles of MnO_4^- = 0.0265 dm^3 x 0.100 mol dm^{-3} = **0.00265 mol**

3. Determine the amount of iron in the reaction
    - From the equation for the reaction, we know the reacting ratio MnO_4^- : Fe^{2+} = 1: 5
    - ∴ moles of Fe^{2+} = 0.00265 mol MnO_4^- x 5 = **0.01325 mol**

4. Convert moles into the mass of iron
    - Mass of iron = 0.01325 mol x 55.85 $gmol^{-1}$ = **0.740 g**

5. Find the percentage of iron in the tablet
    - ∴ % Fe in the tablet = (0.740/ 2.25) x 100 = **32.9%**

Relative Ease of Oxidation & Reduction

Relative Ease of Oxidation & Reduction

- Depending on the position in a group, a metal (in Group 1 or Group 2) will be more or less likely to be oxidised
- When lithium reacts with water hydrogen gas and lithium hydroxide are formed

$$\mathbf{2Li\ (s) + 2H_2O\ (l) \rightarrow 2LiOH\ (aq) + H_2\ (g)}$$

- Lithium is oxidised from Li to Li^+
  - The oxidation number changes from 0 to +1
- This reaction is vigorous, though down Group 1 the reaction becomes even more vigorous and violent
- Therefore down the group, the relative ease of oxidation **increases**
- The same pattern also occurs in Group 2
  - For example, magnesium reacts very slowly with water and calcium reacts much more quickly
    - $Mg\ (s) + 2H_2O\ (l) \rightarrow Mg(OH)_2\ (s) + H_2\ (g)$ = very slow reaction
    - $Ca\ (s) + 2H_2O\ (l) \rightarrow Ca(OH)_2\ (s) + H_2\ (g)$ = very quick reaction

Reduction of Halogens

Oxidising power of the Group 17 elements

- Halogens react with metals by accepting an electron from the metal atom to become an ion with 1– charge

$$Ca\ (s) + Cl_2\ (g) \rightarrow Ca^{2+}(Cl^-)_2\ (s)$$

- Halogens are therefore **oxidising agents**:
- Halogens **oxidise** the metal by removing an electron from the metal (the oxidation number of the metal increases)
- Halogens become **reduced** as they gain an extra electron from the metal atom (the oxidation number of the halogen decreases)
- The **oxidising power** of the halogens **decreases** going **down the group** (the halogens get less reactive)

The relative oxidising power of the halogens

F_2	strongest oxidising agent most readily becomes reduced
Cl_2	↑
Br_2	
I_2	weakest oxidising agent least readily becomes reduced

Reaction of the halogens with halide ions in displacement reactions

- A halogen **displacement** occurs when a **more r**eactive halogen displaces a **less** reactive halogen from an aqueous solution of its halide
- The reactivity of Group 17 non-metals increases as you move up the group
- Out of the 3 halogens, chlorine, bromine and iodine, chlorine is the most reactive and iodine is the least reactive

Aqueous Solution Colour of Halogens

Aqueous solution	Colour
Chlorine	Very pale green, but usually appears colourless as it is very dilute
Bromine	Orange but will turn yellow when very dilute
Iodine	Brown

Halogen displacement reactions

Chlorine and bromine

- If you add chlorine solution to colourless potassium bromide solution, the solution becomes orange as bromine is formed
- Chlorine is **above** bromine in Group 17 so it is more reactive
- Chlorine will therefore **displace** bromine from an aqueous solution of a metal bromide

$$2KBr\,(aq) + Cl_2\,(aq) \rightarrow 2KCl\,(aq) + Br_2\,(aq)$$

potassium bromide + chlorine → potassium chloride + bromine

Bromine and iodine

- Bromine is **above** iodine in Group 17 so it is **more** reactive
- Bromine will therefore **displace** iodine from an aqueous solution of a metal iodide

$$Br_2\,(l) + 2NaI\,(aq) \rightarrow 2NaBr\,(aq) + I_2\,(aq)$$

bromine + sodium Iodide → sodium bromide + iodine

Worked example

Which of the statements below are correct?

I. Potassium chloride solution will react with fluorine to form chlorine.

II. Sodium chloride solution will react with iodine to form chlorine.

III. Lithium iodide solution will react with bromine to form iodine.

A. I and II only

B. I and III only

C. II and III only

D. I, II and III

Answer:

- The correct option is **B**.
  - Fluorine will displace chlorine as it is higher up in the group
  - Bromine will displace iodine for the same reason.
  - Iodine is below chlorine so cannot displace chlorine from sodium chloride

Metal & Metal Ion Reactions

- Metals can be ranked in order of reactivity
    - This is called the **reactivity series** or just **activity series**
- Metals higher in reactivity can **displace** less reactive metals from their compounds in solutions or from their oxides
- An example of a **metal displacement reaction** occurs between magnesium and aqueous copper (II) sulfate solution

$$\mathbf{Mg\ (s) + CuSO_4\ (aq) \rightarrow MgSO_4\ (aq) + Cu\ (s)}$$

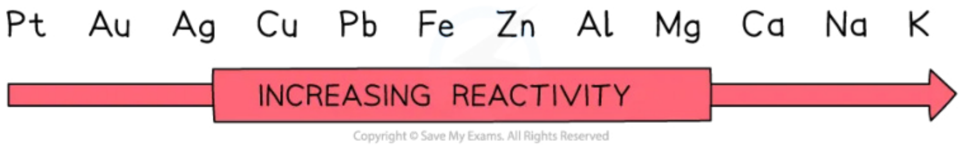
- What are the **redox processes** going on here?
    - If we split the equation into half equations it's easy to see which species is **oxidised** and which is **reduced**:

$$\mathbf{Mg \rightarrow Mg^{2+} + 2e^- \quad \text{Loss of electrons = oxidation}}$$

$$\mathbf{Cu^{2+} + 2e^- \rightarrow Cu \quad \text{Gain of electrons = reduction}}$$

- The more reactive metal acts as a **reducing agent**
- This allows metals to be ranked from most reactive (**strongest reducing agents**) to least reactive:

The metal activity series



The more reactive a metal is the better it is at pushing electrons onto less reactive metal ions. Magnesium is better at pushing electrons onto copper(II) ions than copper is at pushing electrons onto magnesium ions

Worked example

What is the order of decreasing reactivity of the metals (most reactive first)?

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

$Cu (s) + Zn^{2+} (aq) \rightarrow$ No Reaction

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

$Ag (s) + Cu^{2+} (aq) \rightarrow$ No Reaction

A. Zn > Cu > Sn > Ag

B. Sn > Zn > Ag > Cu

C. Ag > Cu > Zn > Sn

D. Zn > Sn > Cu > Ag

Answer:

- The correct option is **D**.
  - The first reaction tells you that zinc is more reactive than tin (Zn > Sn):
    $$Zn (s) + Sn^{2+} (aq) \rightarrow Zn^{2+} (aq) + Sn (s)$$
  - The second reaction tells you that zinc is more reactive than copper (Zn > Cu):
    $$Cu (s) + Zn^{2+} (aq) \rightarrow \text{No Reaction}$$
  - The third reaction tells you that tin is more reactive than copper (Sn > Cu):
    $$Sn (s) + Cu^{2+} (aq) \rightarrow Sn^{2+} (aq) + Cu (s)$$
  - The fourth reaction tells you that copper is more reactive than silver (Cu > Ag):
    $$Ag (s) + Cu^{2+} (aq) \rightarrow \text{No Reaction}$$

Acids with Reactive Metals

Acids with Reactive Metals

Metals and acids

- The typical reaction of a metal and an acid can be summarised as

acid + metal → salt + hydrogen

- For example:

$$\mathbf{2HCl\,(aq) + Zn\,(s) \rightarrow ZnCl_2\,(aq) + H_2\,(g)}$$

hydrochloric acid + zinc → zinc chloride* + hydrogen

$$\mathbf{H_2SO_4\,(aq) + Fe\,(s) \rightarrow FeSO_4\,(aq) + H_2\,(g)}$$

sulfuric acid + iron → iron(II) sulfate* + hydrogen

*zinc chloride and iron(II) sulfate are salts

- A salt is an ionic compound formed when the hydrogen of an acid is replaced by a metal or another positive ion
- Clearly, the extent of the reaction depends on the **reactivity** of the metal and the **strength** of the acid
- Very reactive metals would react dangerously with acids and these reactions are not usually carried out
- Metals low in **reactivity** do not react at all
  - For instance, copper does not react with dilute acids
- **Stronger acids** will react **more vigorously** with metals than weak acids

- What signs of reaction would be expected to be different between the two?
  - Faster reaction seen as:
    - more effervescence
    - the metal dissolves faster

Ionic Equations

- The reactions of acids and metals can be written as ionic equations showing only the species that has changed in the reaction
- Zinc reacts with hydrochloric acid to give a salt and hydrogen
  - Zinc metal is being oxidised to a zin ion as shown in the table

Full equation	$2HCl\,(aq) + Zn\,(s) \rightarrow ZnCl_2\,(aq) + H_2\,(g)$
Ionic equation	$2H^+\,(aq) + Zn\,(s) \rightarrow Zn^{2+}\,(aq) + H_2\,(g)$ $2H^+\,(aq) \cancel{+ 2Cl^-\,(aq)} + Zn\,(s) \rightarrow Zn^{2+}\,(aq) \cancel{+ 2Cl^-\,(aq) +} H_2\,(g)$

Reducing agent	Zn (s) Zn is being oxidised to Zn^{2+} (0 to +2)
Oxidising agent	H^+ (aq) in HCl (aq) H^+ is being reduced to H_2 (+1 to 0)

Table to show the relative reducing power of metals

Mg	**strongest reducing agent – most readily becomes oxidised**
Al	↑
Zn	
Fe	
Pb	
H	
Cu	
Ag	**weakest oxidising agent – least readily becomes oxidised**

Primary Cells

Primary Cells

- We have seen previously that **redox** reactions involve simultaneous **oxidation** and **reduction** as electrons flow from the **reducing agent** to the **oxidising 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

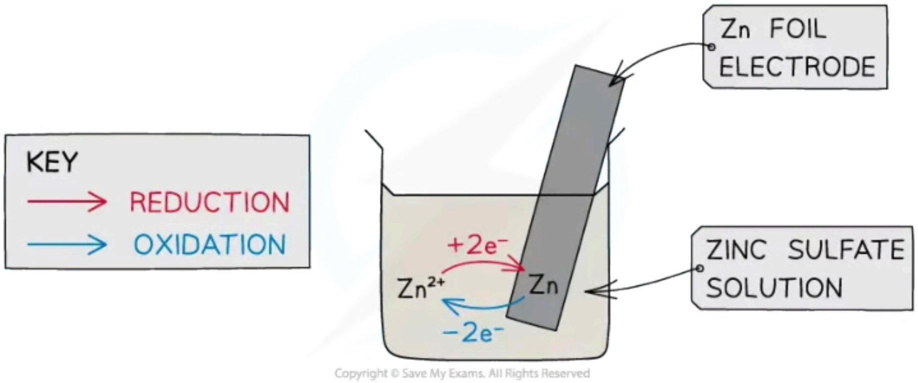
- A **voltaic cell** generates a potential difference known as an **electromotive force** or **EMF**
- The EMF is also called the **cell potential** and is given the symbol ***E***
- The absolute value of a cell potential cannot be determined only the difference between one cell and another
  - This is analogous to arm-wrestling: you cannot determine the strength of an arm-wrestler unless you compare them to the other competitors
- Voltaic (or Galvanic) cells generate electricity from spontaneous redox reactions, e.g.

$$\text{Zn (s)} + \text{CuSO}_4\text{ (aq)} \rightarrow \text{Cu (s)} + \text{ZnSO}_4\text{ (aq)}$$

- 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

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

Zinc metal in a solution of zinc sulfate



When a metal is dipped into a solution containing its ions, an equilibrium is established between the metal and its 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:

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

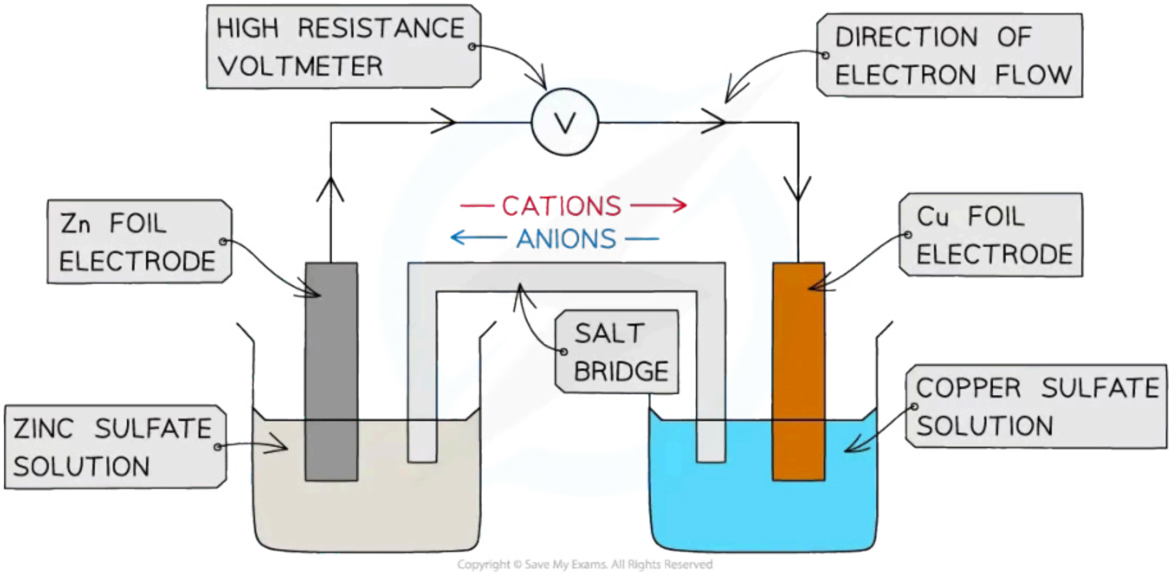
$$Cu(s) \rightleftharpoons Cu^{2+}(aq) + 2e^- \text{ – oxidation (rod becomes negative)}$$

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

Creating an EMF

- 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

Electrochemical cell



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

Conventional Representation of Cells

- Chemists use a type of shorthand convention to represent electrochemical cells
- In this convention:
  - A solid vertical (or slanted) line shows a **phase boundary**, which is an interface between a solid and a solution
  - A double vertical line (sometimes shown as dashed vertical lines) represents **a salt bridge**
    - A salt bridge has mobile ions that complete the circuit
    - Potassium chloride and potassium nitrate are commonly used to make the salt bridge as chlorides and nitrates are usually soluble
    - This should ensure that no precipitates form which can affect the equilibrium position of the half cells
- The substance with the **highest oxidation state** in each half-cell is drawn next to the salt bridge
- The cell potential difference is shown with the **polarity of the right-hand electrode**
- The cell convention for the zinc and copper cell would be

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

- This tells us the copper half-cell is more positive than the zinc half-cell so that electrons would flow from the zinc to the copper
- The same cell can be written as:

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

- The polarity of the right-hand half-cell is negative, so we can still tell that electrons flow from the zinc to the copper half-cell

Worked example

Writing a cell diagram

If you connect an aluminium electrode to a zinc electrode, the voltmeter reads 0.94V and the aluminium is the negative. Write the conventional cell diagram of the reaction.

Answer:

- $\mathrm{Al\ (s)\ |\ Al^{3+}\ (aq)\ \|\ Zn^{2+}\ (aq)\ |\ Zn\ (s)} \qquad E_{cell} = +0.94\ \mathrm{V}$
- It is also acceptable to include phase boundaries on the outside of cells as well:
- $\mathrm{|\ Al\ (s)\ |\ Al^{3+}\ (aq)\ \|\ Zn^{2+}\ (aq)\ |\ Zn\ (s)\ |} \qquad E_{cell} = +0.94\ \mathrm{V}$

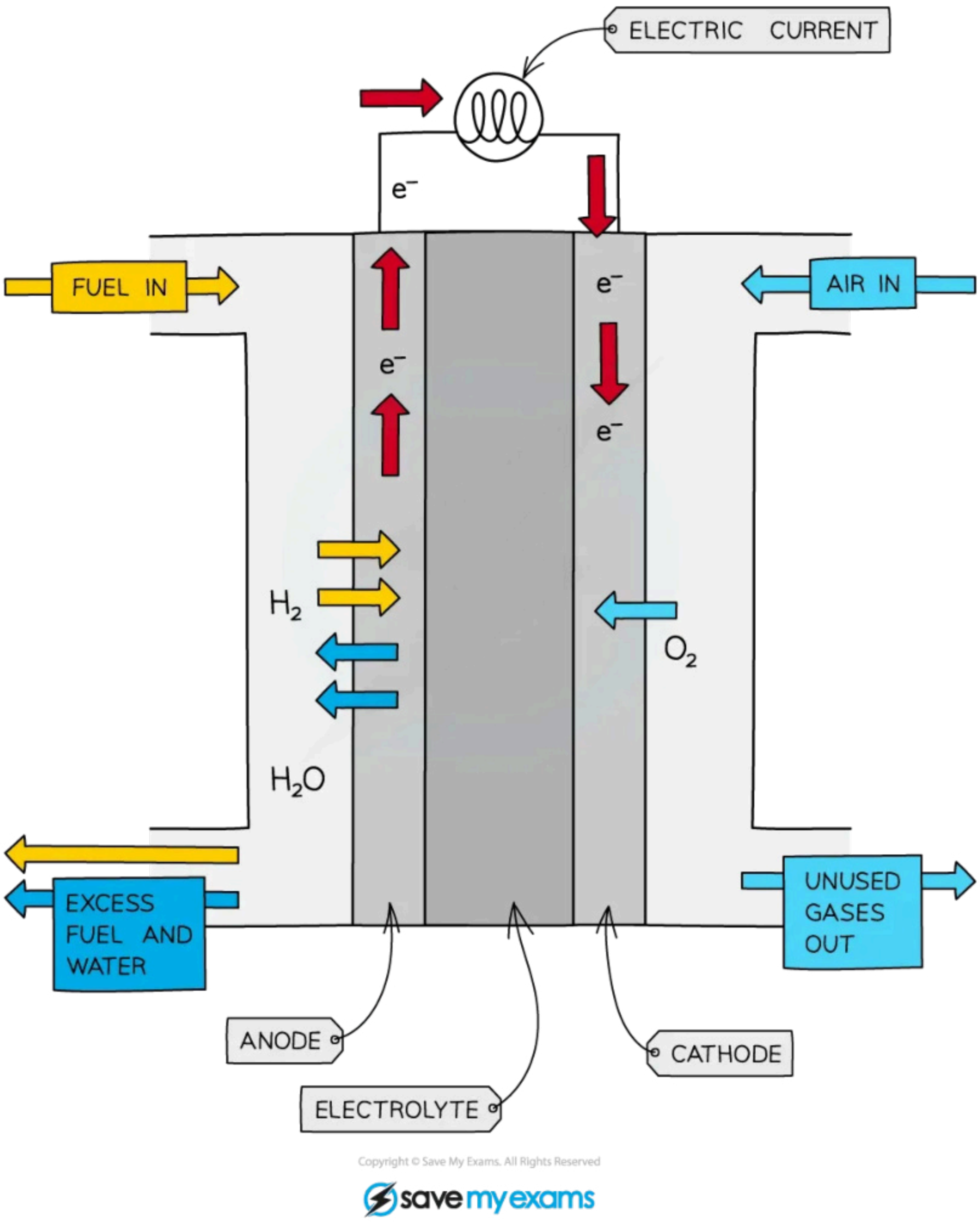
Examiner Tip

- Students often confuse the redox processes that take place in electrochemical cells
    - Oxidation takes place at the negative electrode
    - Reduction takes place at the positive electrode
- Remember, oxidation is the loss of electrons, so you are losing electrons at the negative
- $\mathrm{|\ Al\ (s)\ |\ Al^{3+}\ (aq)\ \|\ Zn^{2+}\ (aq)\ |\ Zn\ (s)\ |} \qquad E_{cell} = +0.94\ \mathrm{V}$

Fuel cells

- A fuel cell is an electrochemical cell in which a fuel **donates** electrons at one electrode and oxygen **gains** electrons at the other electrode
- These cells are becoming more common in the automotive industry to replace petrol or diesel engines
- As the fuel enters the cell it becomes oxidised which sets up a **potential difference** or voltage within the cell
- Different electrolytes and fuels can be used to set up different types of fuel cells
- An important cell is the **hydrogen-oxygen** fuel cell which combines both elements to release energy and water

The hydrogen-oxygen fuel cell



A hydrogen-oxygen fuel cell combines both elements to release energy and water

- The fuel cell consists of
    - A reaction chamber with separate inlets for hydrogen and oxygen gas
    - An outlet for the product - water
    - An electrolyte of aqueous sodium hydroxide

  - A semi-permeable membrane that separates the hydrogen and oxygen gases
- The half equations are

$$2H_2\,(g) + 4OH^-\,(aq) \rightarrow 4H_2O\,(l) + 4e^- \qquad E^\theta = -0.83\ V$$

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

- The overall reaction is found by combining the two half equations and cancelling the common terms:

$$2H_2\,(g) + 4OH^-\,(aq) + O_2\,(g) + 2H_2O + 4e^- \rightarrow 4H_2O\,(l) + 4e^- + 4OH^-\,(aq)$$

$$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(l) \qquad E^\theta = +1.23\ V$$

Benefits of fuel cells

- Water is the only reaction product, so fuel cells present obvious environmental advantages over other types of cells
- The reaction is the same as hydrogen combusting in oxygen, but since the reaction takes place at room temperature without combustion, all the bond energy is converted into electrical energy instead of heat and light
- There are no harmful oxides of nitrogen produced, which are usually formed in high-temperature combustion reactions where air is present
- Fuel cells have been used on spacecraft, where the product can be used as drinking water for astronauts

Risks and problems of fuel cells

- Hydrogen is a highly flammable gas and the production and storage of hydrogen carries safety hazards
- Very thick walled cylinders and pipes are needed to store hydrogen which has economic impacts
- The production of hydrogen is a by-product of the crude oil industry, which means it relies on a **non-renewable, finite resource**
- Until a cheap way is found to make hydrogen, its widespread use in fuel cells will be limited
- Hydrogen has high energy density, that is, the amount of energy contained in 1g of the fuel is high compared to other fuels, but because it is a gas, its energy density per unit volume is low which means larger containers are needed compared to liquid fuels

Examiner Tip

- One difference between fuel cells and other cells is that the cell operates continuously as long as there is a supply of hydrogen and oxygen
  - The energy is not stored in the cell

Redox in Voltaic Cells

- Electrochemical cells can be either **voltaic** (galvanic) or **electrolytic** cells
  - Voltaic cells generate electricity from chemical reactions
    - This is a spontaneous reaction which drives electrons around a circuit
  - Electrolytic cells drive chemical reactions using electrical energy
    - An electric current reverses the normal directions of chemical change and this is non-spontaneous
    - Stable compounds such as sodium chloride or lead bromide can be broken down into their elements
- Oxidation takes place at the anode and reduction will occur at the cathode
  - Depending on the type of cell, the polarity changes
    - In voltaic cells the anode is negative
    - In electrolytic cells the anode is positive

Comparing Voltaic & Electrolytic Cells Summary Table

	Negative	**Positive**
Voltaic cell	anode	cathode
	oxidation	reduction
Electrolytic cell	cathode	anode
	reduction	oxidation

Examiner Tip

- Students often confuse the redox processes that take place in voltaic cells and electrolytic cells
- An easy way to remember is the phrase **RED CAT**:
  - **RED**uction takes place at the **CAT**hode!

Secondary Cells

Secondary Cells

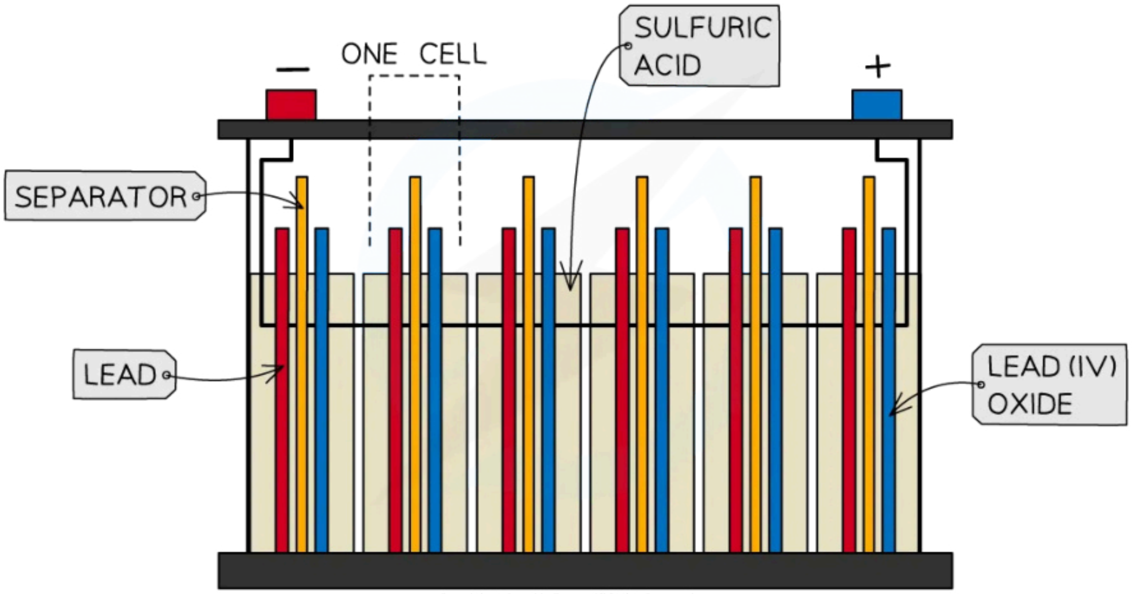
Secondary Cells

- Secondary / rechargeable cells employ chemical reactions which can be reversed by applying a voltage greater than the cell voltage, causing electrons to push in the opposite direction
- There are many types of rechargeable cells, but common ones include:
  - **Lead-acid** batteries,
  - **Nickel-cadmium / NiCad** cells
  - **Lithium** cells

Lead-acid batteries

- Lead-acid batteries consist of **six cells** joined together **in series**
- The cells use **lead** metal as the **negative electrode** and **lead(IV) oxide** as the **positive electrode**
- The electrolyte is sulfuric acid

A lead-acid battery



A lead acid battery is made by placing negative lead and positive lead dioxide electrodes into the sulfuric acid electrolyte

- The half-cell reactions are

$$Pb\,(s) + SO_4^{2-}\,(aq) \rightarrow PbSO_4\,(s) + 2e^- \qquad E^\theta = -0.36\ V$$

$$PbO_2\,(s) + 4H^+\,(aq) + SO_4^{2-}\,(aq) + 2e^- \rightarrow PbSO_4\,(s) + 2H_2O\,(l) \qquad E^\theta = +1.70\ V$$

- The cell generates an EMF of about 2 V and the overall reaction is

$$PbO_2\,(s) + 4H^+\,(aq) + 2SO_4^{2-}\,(aq) + Pb\,(s) \rightarrow 2PbSO_4\,(s) + 2H_2O\,(l) \qquad E^\theta_{cell} = +2.06\ V$$

- In a commercial car battery, the six cells in series give a combined voltage of about 12 V
  - When the car is in motion, the generator provides a push of electrons that reverses the reaction and regenerates lead and lead(IV) oxide
- Lead-acid batteries are designed to produce a **high current** for a short period of time, hence their use in powering a starter motor in car engines
- The disadvantage of lead-acid batteries is that:
  - They are very **heavy**
  - They contain **toxic** materials: lead and lead(IV) oxide
  - The sulfuric acid electrolyte is very **corrosive**
- This presents challenges of disposal when lead-acid batteries come to the end of their useful life

NiCad cells

- Nickel-cadmium cells are available in many standard sizes and voltages so they can replace almost any application of traditional zinc-carbon cells
- Although they are more expensive cells, the fact they can be recharged hundreds of times means they are commercially viable
- The negative electrode consists of cadmium and the positive electrode is made of a nickel(II) hydroxide-oxide system
- The half-cell reactions are

$$Cd\,(s) + 2OH^-\,(aq) \rightarrow Cd(OH)_2\,(s) + 2e^- \qquad E^\theta = -0.82\ V$$

$$NiO(OH)\,(s) + H_2O\,(l) + e^- \rightarrow Ni(OH)_2\,(s) + OH^-\,(aq) \qquad E^\theta = +0.38\ V$$

- The overall reaction in the cell is

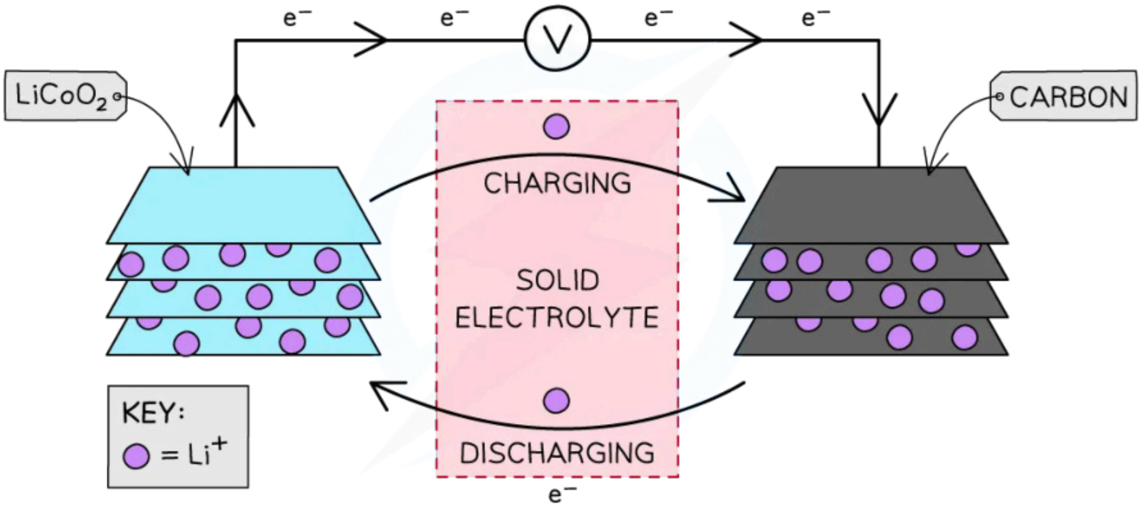
$$2NiO(OH)\,(s) + 2H_2O\,(l) + Cd\,(s) \rightarrow 2Ni(OH)_2\,(s) + Cd(OH)_2\,(s) \qquad E^\theta = +1.2\ V$$

- Cadmium is a toxic metal so the disposal of old NiCad cells is also an environmental issue

Lithium-ion cell

- Lithium ion cells power the laptop or mobile device you are probably reading this on
- The Noble Prize for Chemistry in 2019 was awarded to John B. Goodenough, M. Stanley Whittingham and Akira Yoshino for their work on lithium ion cells that have revolutionised portable electronics
- Lithium is used because it has a very low density and relatively high electrode potential
- The cell consists of:
  - A positive lithium cobalt oxide electrode
  - A negative carbon electrode
  - A porous polymer membrane electrolyte
- The polymer electrolyte cannot leak since it is not a liquid or paste, which presents advantages over other types of cells

Lithium-ion cell



The lithium-ion cell consists of a positive lithium cobalt oxide electrode and a negative carbon electrode

- The cell consists of a sandwich of different layers of lithium cobalt oxide and carbon
- When the cell is charged and discharged the lithium ions flow between the negative and the positive through the solid electrolyte
- The half-cell reactions on discharge are:

$$\text{Li (s)} \rightarrow \text{Li}^+\text{(s)} + e^- \qquad E^\theta = -3\text{ V}$$

$$\text{Li}^+\text{(s)} + \text{CoO}_2\text{(s)} + e^- \rightarrow \text{Li}^+(\text{CoO}_2)^-\text{(s)} \qquad E^\theta = +1\text{ V}$$

- The cell generates an EMF of between 3.5 V and 4.0 V and the overall reaction is

$$\text{Li (s)} + \text{CoO}_2\text{(s)} \rightarrow \text{Li}^+(\text{CoO}_2)^-\text{(s)} \qquad E^\theta_{cell} \sim +3.5$$

- NiCad cells have a problem called the memory effect in which they gradually begin to lose their charge after repeated charge cycles when the cell is not fully discharged. The cells appear to 'remember' their lower state of charge
- Lithium-ion cells do not have this problem so can be topped up without any loss of charge
- Some of the problems with lithium-ion cells:
    - A global shortage of lithium is likely to make lithium-ion cells unsustainable as the current demand for lithium exceeds the supply
    - If cells are not recycled but thrown away in landfills, then a huge amount of lithium becomes lost to future generations
    - Reports of lithium-ion cell fires have raised concern about the safety of these batteries in electronic devices; it is a reminder to us that lithium is a very reactive element in Group 1 of the periodic table, which is why it has a high electrode potential

Summary of primary and secondary cells

Type of cell	Advantages	Disadvantages

Primary	**General**	Inexpensive Lightweight Long shelf life	Single-use which increases landfill and causes environmental impacts Only delivers small currents
	Fuel cell	Reduced pollution if hydrogen used as fuel Hydrogen has a low density More efficient than combustion as more chemical energy converted to electrical energy	Safety issues with hydrogen gas Hydrogen must be transported using heavy containers Expensive Only delivers small currents Technical issues due to catalytic failures, leaks and corrosion
Rechargeable / secondary	**General**	Materials can be regenerated Can deliver high current	
	Lead-acid	Can deliver large amounts of energy over short periods	Heavy mass Lead and sulfuric acid could cause pollution
	Cadmium-nickel	Longer life than lead-acid batteries	Cadmium is very toxic Produces a low voltage Expensive
	Lithium-ion	Low density of lithium No toxic heavy metals High voltage	Limited life span Expensive

Electrolytic Cells

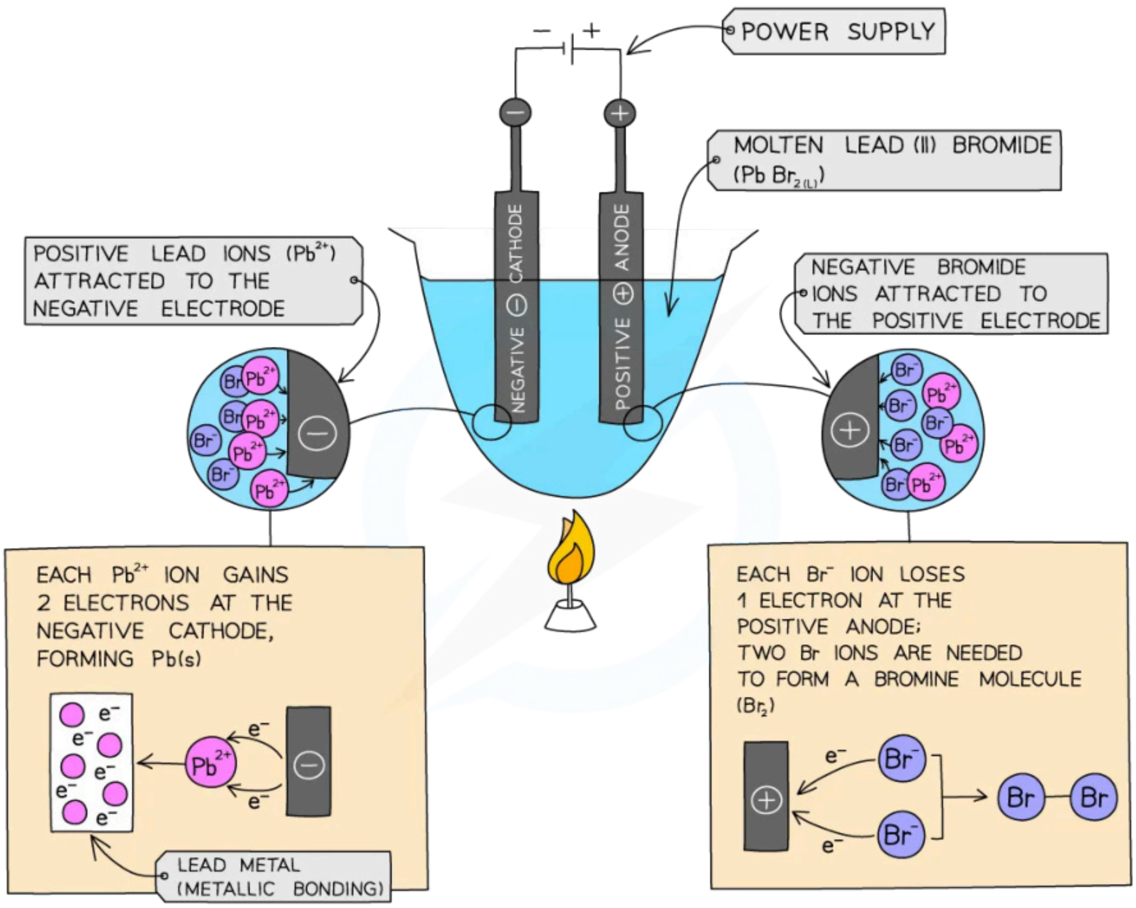
Electrolytic Cells

- An ionic compound conducts electricity when it is molten or in solution
- The current causes the ionic compound to split up and form new substances.
- This process is called **electrolysis**, a word which comes from Greek and means "splitting by electricity"
- **Electrolysis** has many uses, including:
  - Purifying copper
  - Plating metals with silver and gold
  - Extracting reactive metals, such as aluminium
  - Making chlorine, hydrogen and sodium hydroxide

Electrolytic cells

- Electrolytic cells can be constructed using a beaker or crucible as the cell depending on whether the ionic compound is in solution or molten

Lead bromide electrolytic cell



Electrolysis of a binary ionic compound, when molten, produces the component elements

- In electrolysis, the substance that the current passes through and splits up is called the **electrolyte**
- The electrolyte contains positive and negative ions

What happens to the ions during electrolysis?

- **Negative ions** move to the **anode** and lose electrons - this is **oxidation**
- **Positive ions** move to the **cathode** and gain electrons - this is **reduction**
- Electrically neutral atoms or molecules are released

Electrolysis of molten lead bromide

- The reactions which take place at the electrodes can be shown by half equations
- When the positive lead ions move to the **cathode**, they gain electrons in a **reduction** reaction:

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

- Similarly, when the negative bromide ions move to the **anode** they lose electrons in an **oxidation** reaction:

$$2Br^-(l) - 2e^- \rightleftharpoons Br_2\ (l)$$

- Sometimes oxidation reactions are written with '+2e⁻' on the right of the arrow instead of '-2e' on the left
- In this case, the alternative half equation is:

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

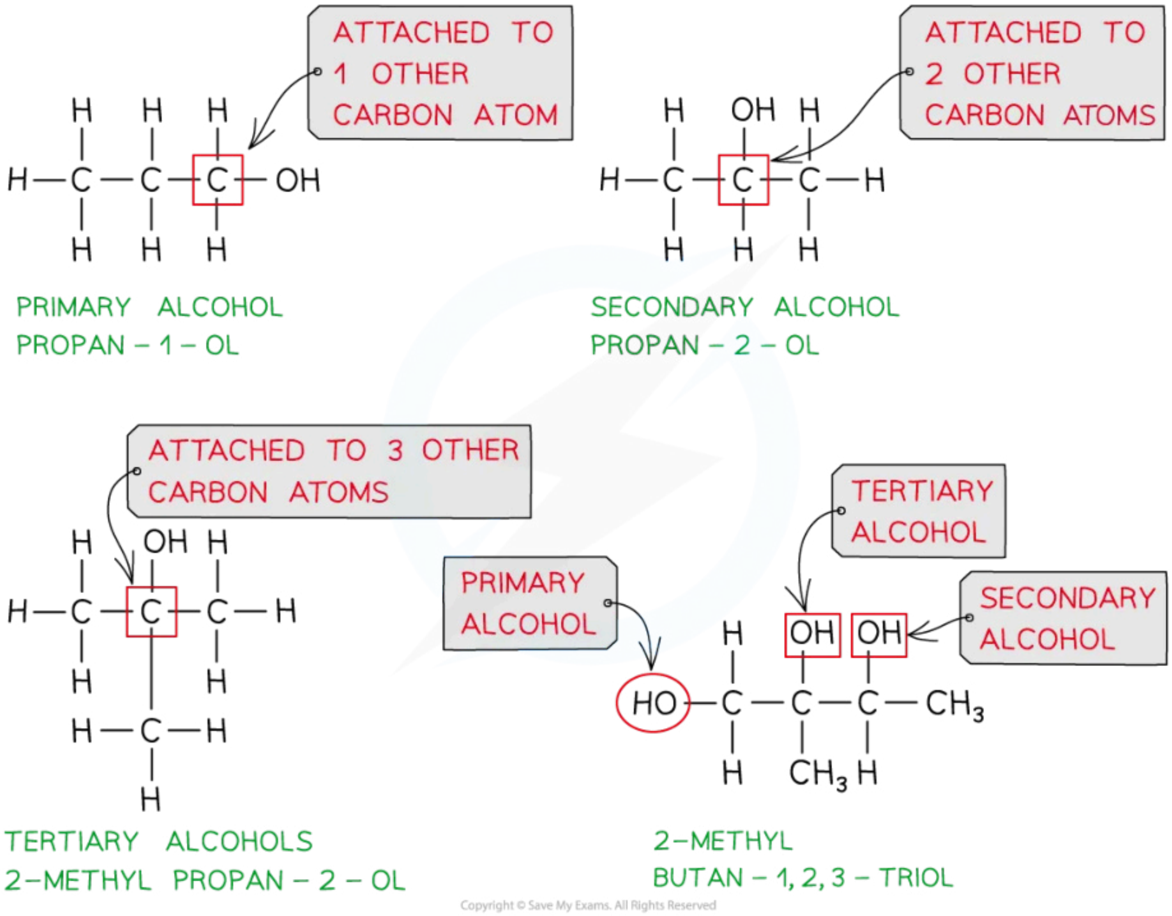
- Since metals are always **cations** and non-metal **anions**, it is easy to predict the products of electrolysis of molten salts:
  - **Metals** will always be formed at the **cathode** and **non-metals** at the **anode**

Oxidation of Alcohols

Oxidation of Alcohols

- The products of oxidation of **alcohols** depends on the class of **alcohols**
- Here is a reminder of the three classes of alcohols:

The three classes of alcohols



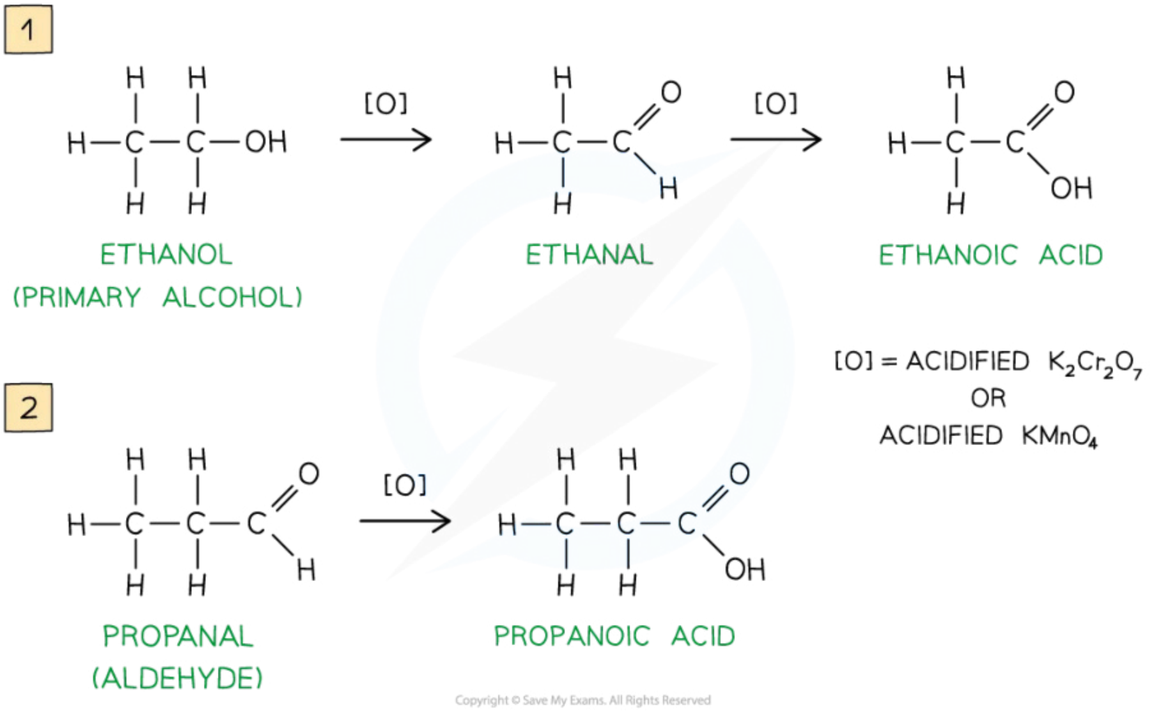
Classification of primary, secondary and tertiary alcohols

Primary alcohols

- **Primary alcohols** can be oxidised to form **aldehydes** which can undergo further oxidation to form **carboxylic acids**
- The oxidising agents of alcohols include **acidified $K_2Cr_2O_7$** or **acidified $KMnO_4$**
- **Acidified potassium dichromate(VI)**, $K_2Cr_2O_7$, is an orange oxidising agent

  - Acidified means that the potassium dichromate(VI) is in a solution of **dilute acid** (such as dilute sulfuric acid)
  - For potassium dichromate(VI) to act as an oxidising agent, it itself needs to be reduced
    - When alcohols are **oxidised** the orange dichromate ions ($Cr_2O_7^{2-}$) are reduced to green Cr^{3+} ions
- **Acidified potassium manganate(VII)**, $KMnO_4$, is a purple oxidising agent
  - As with acidified $KMnO_4$, the potassium manganate(VII) is in an acidic medium to allow the reduction of potassium manganate(VII) to take place
    - When alcohols are **oxidised,** the purple manganate ions (MnO_4^-) are reduced to colourless Mn^{2+} ions

Diagram to show the oxidation of of primary alcohols



A primary alcohol can be oxidised to an aldehyde and then carboxylic acid

Further Oxidation

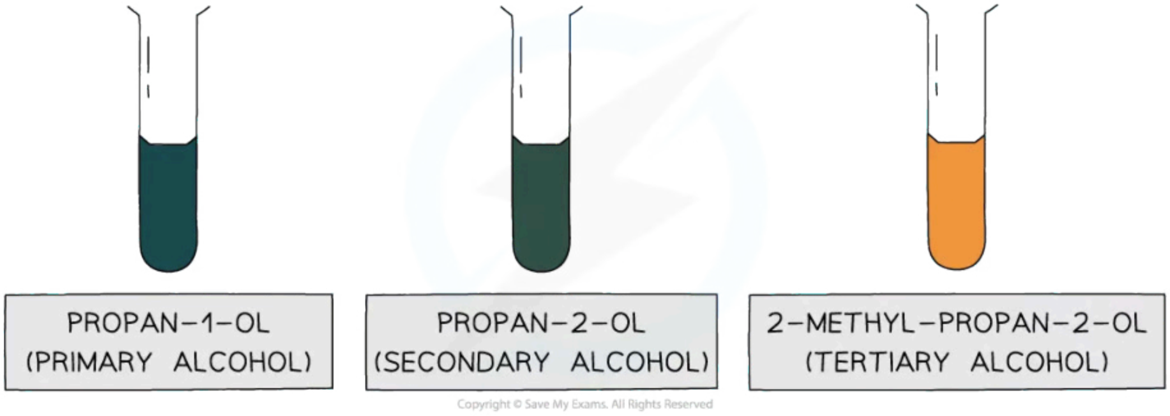
- If the **aldehyde** is not distilled off, further oxidation with **excess** oxidising agent will oxidise it to a **carboxylic acid**
- The reaction takes some time to complete and requires sustained heating

Test for alcohols

- The oxidation using **acidified potassium dichromate(VI)** provides the basis for the test for **alcohols** as the reaction gives a strong colour change from **orange to green**

- Unfortunately, it does not work for tertiary alcohols, which cannot be oxidised

The test for primary and secondary alcohols

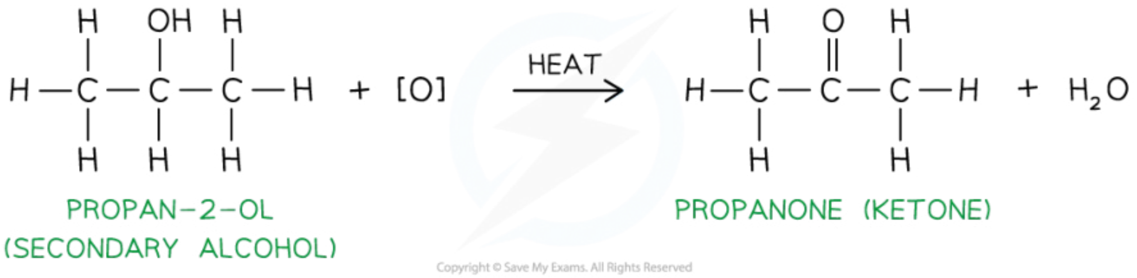


When primary, secondary and tertiary alcohols are reacted with acidified potassium dichromate(VI), primary and secondary alcohols cause a colour change from orange to green. There is no reaction with tertiary alcohols so the colour remains orange

Oxidation of Secondary Alcohols

- **Secondary alcohols** can be oxidised to form **ketones** only
- To get a good yield of the **ketone** the reaction requires some sustained heating

Oxidation of secondary alcohols



Secondary alcohols oxidise to form ketones

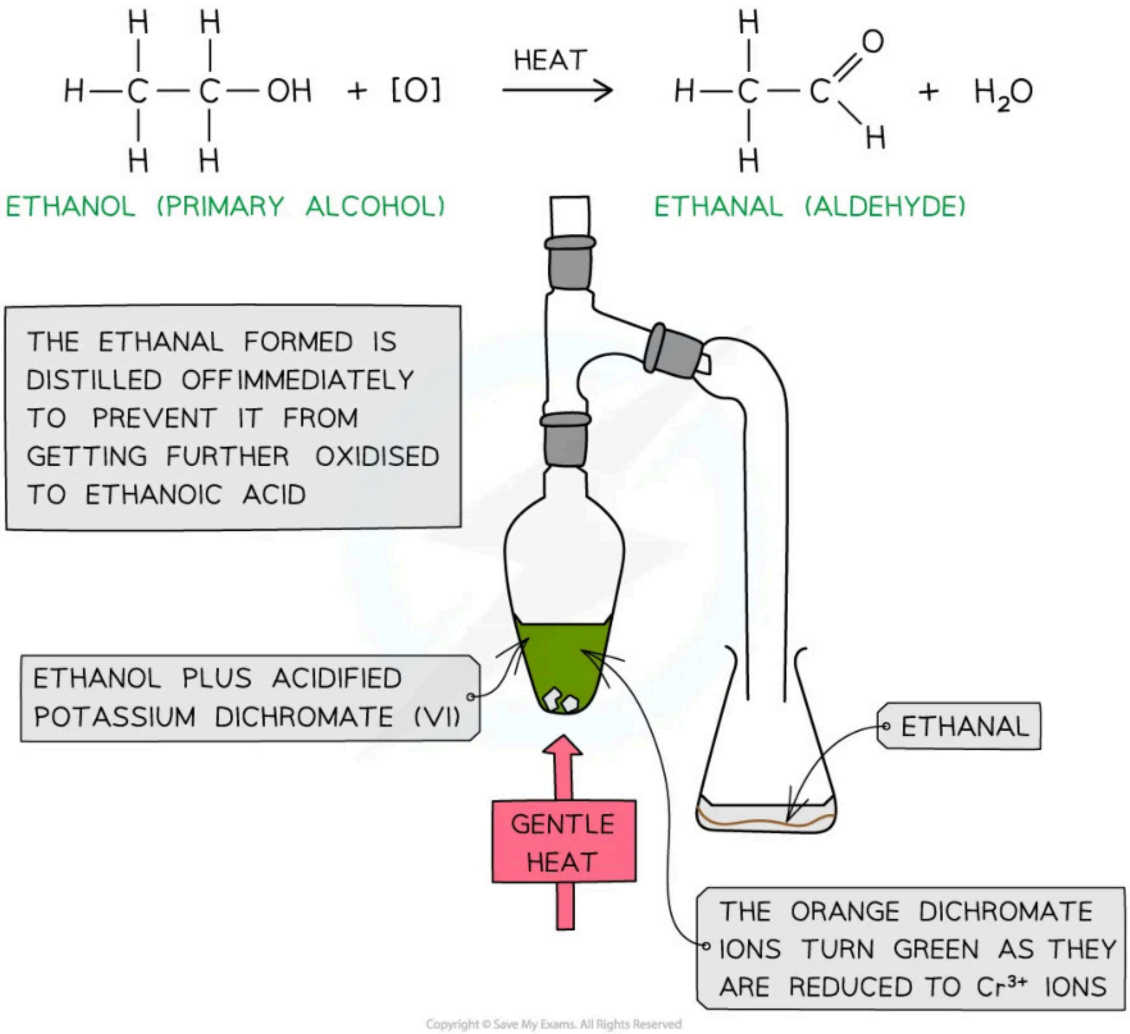
- **Tertiary alcohols** do not undergo oxidation
  - This is because there must be a hydrogen on the functional group carbon, which breaks off to form water
  - There are only **C–C** bonds on the functional group carbon in a **tertiary alcohol**

Distillation & Reflux

Distillation

- To produce an aldehyde from a primary alcohol the reaction mixture must be heated
- The **aldehyde** product has a lower boiling point than the **alcohol** (since it has lost the **H-bonding**) so it can be **distilled off** as soon as it forms
- **Distillation** can be carried out using a simple side arm arrangement which acts as an air condenser or the vapours can be made to pass through a condenser

Diagram of distillation apparatus



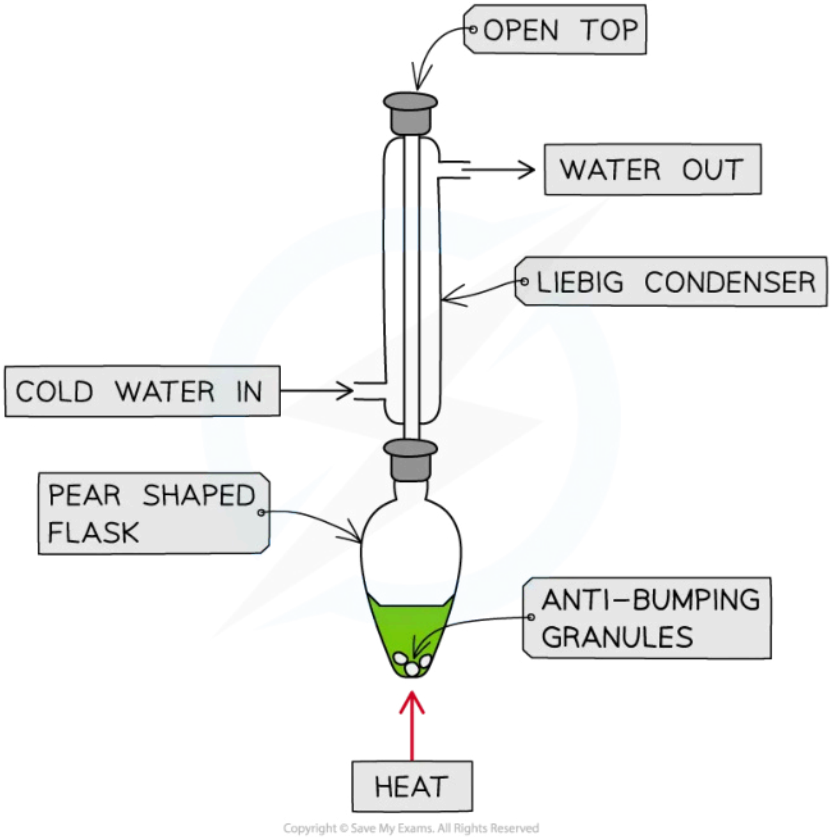
Oxidation of ethanol by acidified $K_2Cr_2O_7$ to form an aldehyde by distillation

Heating under reflux

- For reactions that require sustained heating the apparatus has to be modified

- To prevent loss of volatile reactants the apparatus includes a condenser in the vertical position which returns components back into the reaction flask
- This is known as **heating under reflux** (reflux means re-boiling)

Diagram of reflux apparatus



Heating under reflux requires the condenser to be set up vertically

Reduction of Carboxylic Acids, Aldehydes & Ketones

Reduction of Carboxylic Acids, Aldehydes & Ketones

Carbonyl compounds

- Alcohols can be oxidised to carbonyl compounds in the presence of a suitable oxidising agent
  - Primary alcohol → aldehyde → carboxylic acid
  - Secondary alcohol → ketone
  - Tertiary alcohol - no reaction
- These reactions can be reversed in the presence of a suitable reducing agent
  - Carboxylic acid → aldehyde → primary alcohol
  - Ketone → secondary alcohol
- The two most common reducing agents for carbonyl compounds are:
  - Lithium aluminium hydride, $LiAlH_4$, in anhydrous conditions, commonly dry ether, followed by the addition of aqueous acid
    - This is the stronger of these reducing agents and can reduce carboxylic acids
  - Sodium borohydride, $NaBH_4$, in aqueous or alcoholic solutions
    - This is the less hazardous of these reducing agents but it cannot reduce carboxylic acids
  - Both of these reagents produce the nucleophilic hydride ion, H^-

Examiner Tip

- You can be expected to know typical conditions and reagents of all reactions, e.g. catalysts, reducing agents, reflux, etc
- However, you do not need to know more precise details such as specific temperatures

Reduction Reactions

- Equations for reduction reactions can be written using [H] to represent the reducing agent

Carboxylic acids

- Carboxylic acids are reduced to primary alcohols
  - This requires heating with $LiAlH_4$ under reflux in dry ether followed by dilute acid
  - Remember that $NaBH_4$ cannot reduce carboxylic acids

Reduction of a carboxylic acid

Carboxylic acids are reduced to primary alcohols with LiAlH$_4$

Aldehydes

- Aldehydes are reduced to primary alcohols
    - This can be with LiAlH$_4$ or NaBH$_4$

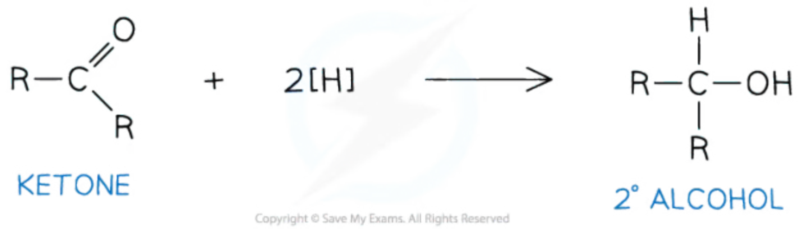
Reduction of an aldehyde

Aldehydes are reduced to primary alcohols with LiAlH$_4$ or NaBH$_4$

Ketones

- Ketones are reduced to secondary alcohols
    - This can be with LiAlH$_4$ or NaBH$_4$

Reduction of a ketone



Ketones are reduced to secondary alcohols with LiAlH$_4$ or NaBH$_4$

Examiner Tip

- Take care if you are asked about the formation of an aldehyde from a carboxylic acid
    - You have to use $LiAlH_4$ refluxed in dry ether, followed by dilute acid
    - This reaction cannot be stopped at the aldehyde because the $LiAlH_4$ is too powerful
- To form an aldehyde from a carboxylic acid, you have to reduce the carboxylic acid down to a primary alcohol and then oxidise it back up to the aldehyde

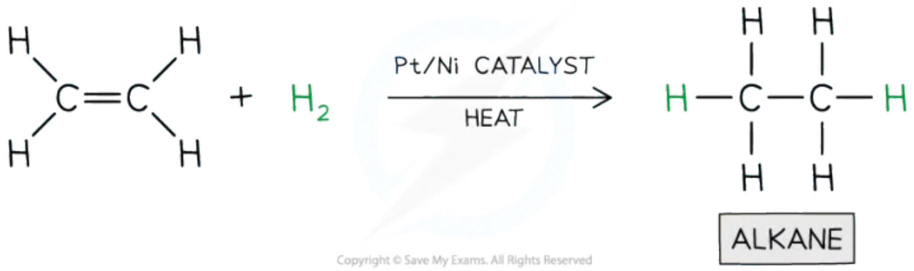
Reduction of Unsaturated Compounds

Reduction of Unsaturated Compounds

Reduction of alkenes

- **Alkenes** are very useful compounds as they can undergo many types of reactions
- They can therefore be used as starting molecules when making new compounds
- The reaction between an **alkene** and hydrogen is known as **hydrogenation** or **reduction**
- As well as a **nickel catalyst**, this requires a temperature of 200 °C and a pressure of 1000 kPa

The reduction of ethene to ethane

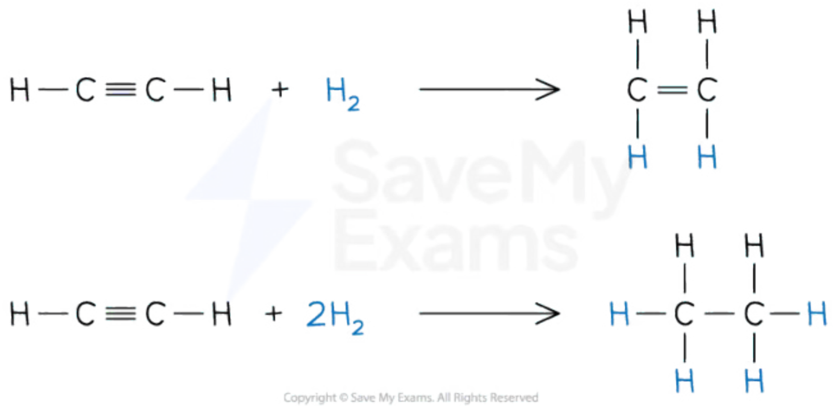


Catalytic hydrogenation converts alkenes into useful alkanes

Reduction of alkynes

- Similarly, alkynes, C_nH_{2n-2} , can be reduced to alkenes, C_nH_{2n} , and alkanes, C_nH_{2n+2}
- The number of molecules of hydrogen needed to convert the organic molecule to the corresponding saturated molecule is related to the number of multiple bonds in the molecule.

Reduction of alkynes to alkenes and alkanes



Alkenes require one molecule of hydrogen to be converted to an alkane. Alkynes require two molecules of hydrogen to be converted to an alkane

- One important application of this reaction is in the production of margarine from vegetable oils
- Vegetable oils are **unsaturated** and may be **hydrogenated** to make margarine, which has a higher melting point due to stronger **London Dispersion Forces**
- By controlling the conditions it is possible to restrict how many of the C=C bonds are broken and produce **partially hydrogenated vegetable oils** which have the desired properties and textures for margarine manufacture

The Hydrogen Electrode (HL)

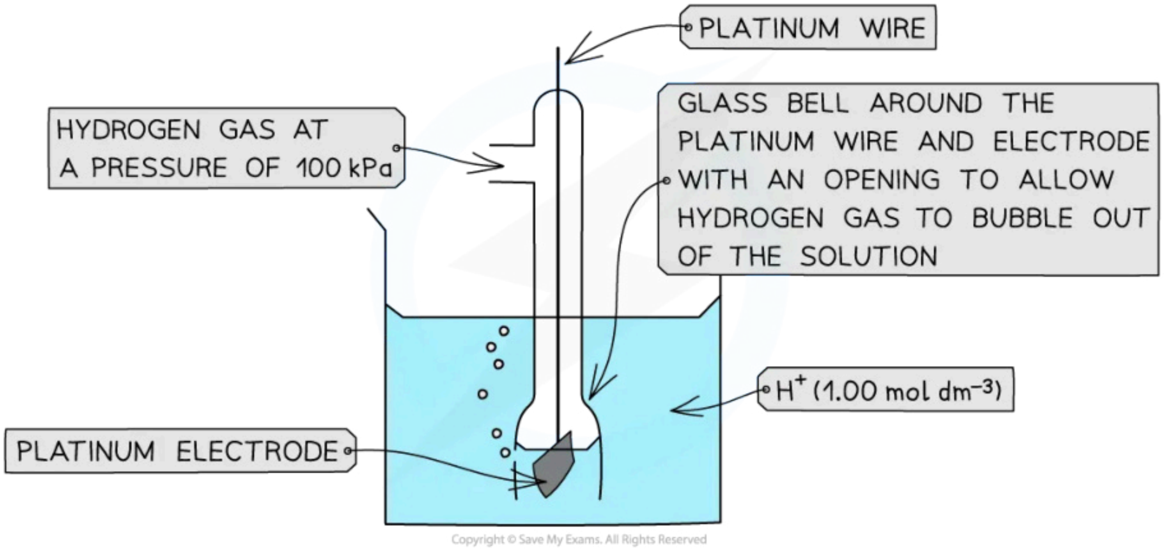
The Hydrogen Electrode

- 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 $E^\theta = 0.00$ 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

Standard hydrogen electrode diagram



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:

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

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

- 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

- 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

Examiner Tip

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

Reduced state to an oxidised state – oxidised state to a reduced state (ROOR)

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 ≣ Oxidised ‖ Oxidised≣Reduced

Pt ≣Fe^{2+}(aq), Fe^{3+}(aq) ‖ Cl_2 (g), 2Cl^- (aq) ≣Pt

Standard Cell Potentials (HL)

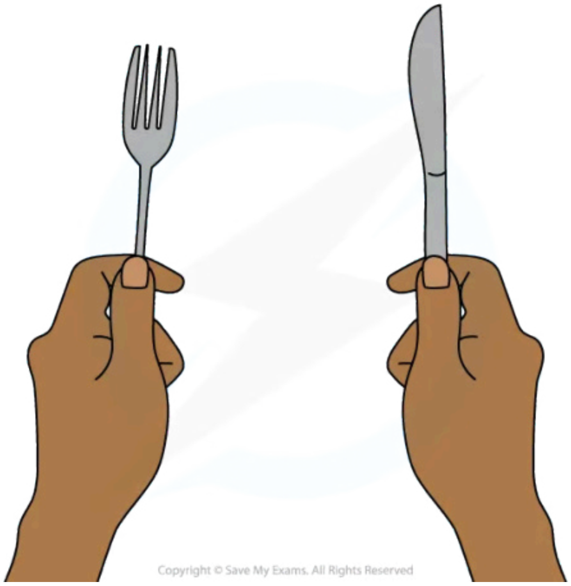
Standard Cell Potentials

- Voltmeters measure the 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'

Trick to remember how to calculate EMF



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

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

  - The $Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ half-cell thus has an electrode potential of -0.76V
- If the $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ electrode is connected to the standard hydrogen electrode and the standard hydrogen electrode is placed on the left, the voltmeter reads +0.34V
  - The $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ half-cell thus has an electrode potential of +0.34V

Standard electrode potential

- 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.

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

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

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

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

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

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

Determining the direction of spontaneity

- 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:

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

- 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:

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

Worked example

Using data from Section 19 of the Data Book, determine if the reaction shown is spontaneous at standard conditions

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

Section 19 of the Data Book shows the following half-reactions:

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

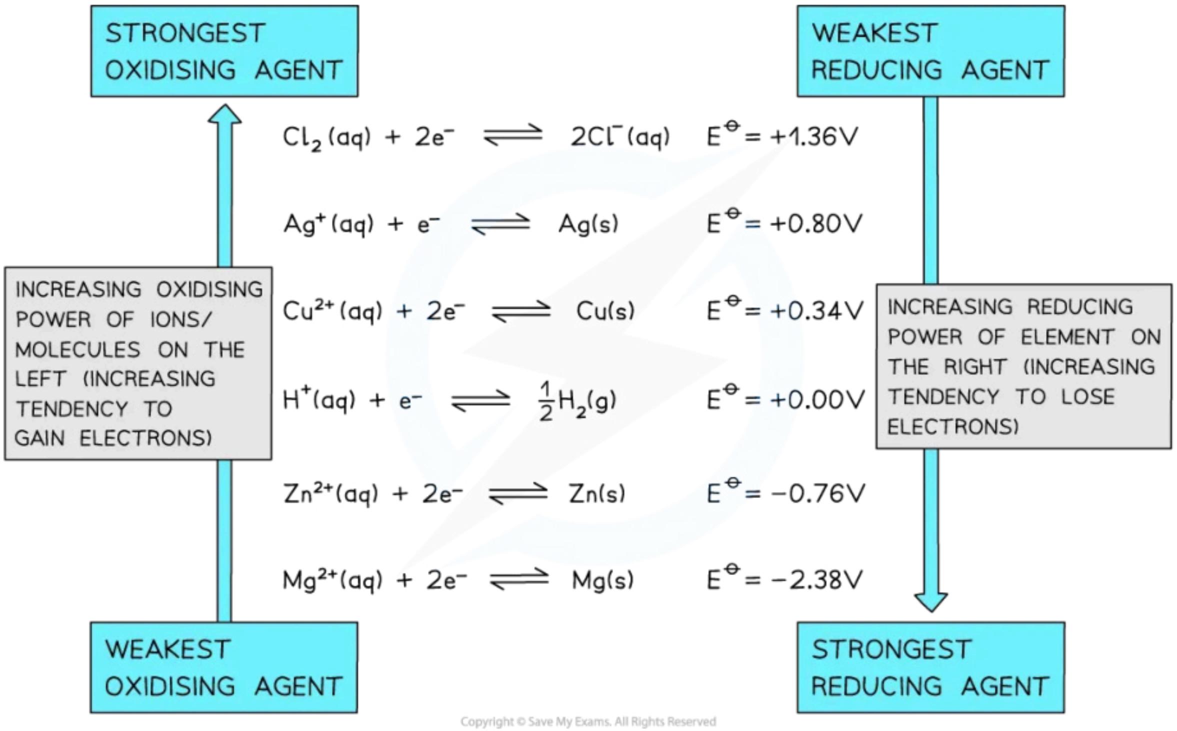
$Mn^{2+}\,(aq) + 2e^- \rightarrow Mn\,(s)$ $E^{\theta} = -1.18\ V$

Answer:

- Manganese is the more negative value, so will be E_{LHS} or $E_{oxidation}$ in the spontaneous reaction
- EMF $= E_{RHS} - E_{LHS} = (-0.14) - (-1.18) = +1.04$
- For oxidation to take place, the manganese must lose electrons and the tin(II) must gain electrons
- $Mn\,(s) \rightarrow Mn^{2+}\,(aq) + 2e^-$ and $Sn^{2+}\,(aq) + 2e^- \rightarrow Sn\,(s)$
- So, the spontaneous reaction is
- $Mn\,(s) + Sn^{2+}\,(aq) \rightarrow Mn^{2+}\,(aq) + Sn\,(s)$
- Therefore, the reaction in the question is **not** spontaneous

- The $E^{\ominus}$ values of a species indicate how **easily** they can get **oxidised** or **reduced**
- In other words, they indicate the relative **reactivity** of elements, compounds and ions as **oxidising agents** or **reducing agents**
- The **electrochemical series** is a list of various **redox equilibria** in order of decreasing $E^{\ominus}$ values
- **More positive** (less negative) $E^{\ominus}$ values indicate that:
  - The species is easily **reduced**
  - The species is a better **oxidising agent**
- **Less positive** (more negative) $E^{\ominus}$ values indicate that:
  - The species is easily **oxidised**
  - The species is a better **reducing agent**

Diagram to show the trends in oxidising and reducing power



Metals with the most negative E^θ values are the strongest reducing agents and non-metals with the more positive E^θ values are the strongest oxidising agents

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 of 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'

Gibbs Energy & Standard Cell Potential (HL)

Gibbs Energy & Standard Cell Potential

- 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:

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

- 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 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
  - ΔG^{θ} = **- 212300 J mol^{-1}** 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
ΔG^{θ} = -ve	E^{θ} = +ve	The reaction is spontaneous
ΔG^{θ} = +ve	E^{θ} = -ve	This reaction is non-spontaneous
ΔG^{θ} = 0	E^{θ} = 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

Electrolysis of Aqueous Solutions (HL)

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 sulfate solution with inert electrodes	Copper	Oxygen

Copper sulfate 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:

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

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

- 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:

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

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

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

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

- 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):

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

- 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:

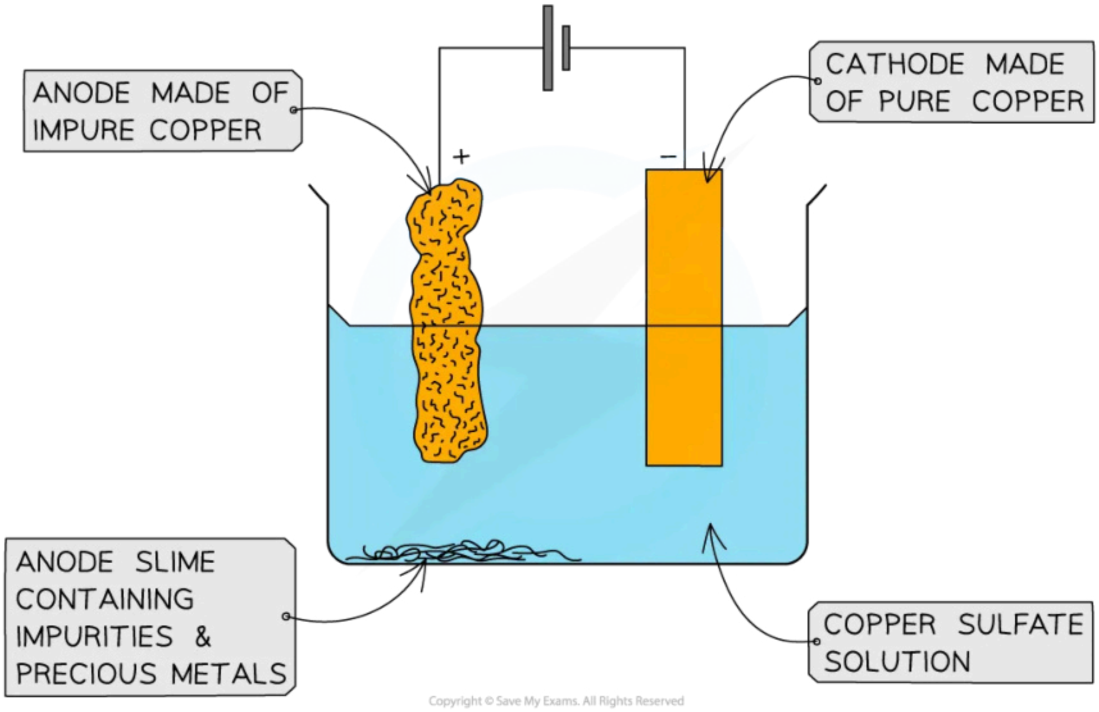
$$Cu^{2+} (aq) + 2e^- \rightarrow Cu (s) \qquad E^\theta = +0.34 \text{ V}$$

- However, at the anode, the copper electrode is oxidised and dissolves to form copper ions

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

- 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

Diagram to show the purification of copper via electrolysis



The purification of copper by electrolysis

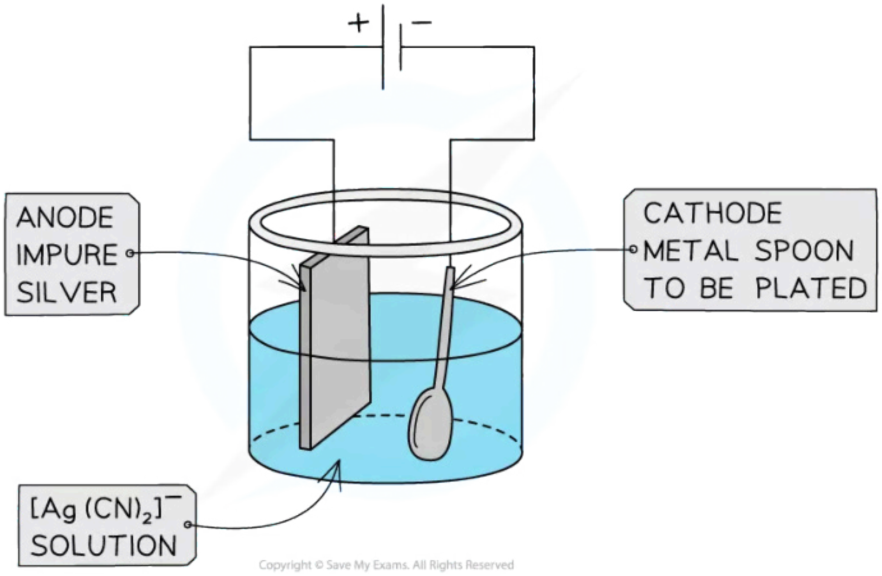
- The anode slowly dissolves away and the cathode builds up pure copper
- The impurities form a slime under the anode which is actually quite valuable as it often contains significant quantities of precious metals like silver

Electroplating (HL)

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, e.g.
    - Gold-plated jewellery is made for aesthetic reasons
    - Iron is galvanized with zinc to protect the iron from rusting

Diagram showing the process of electroplating a metal spoon



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 embedded with metallic particles that conduct electricity and can then be metal plated