Cambridge (CIE) IGCSE Chemistry

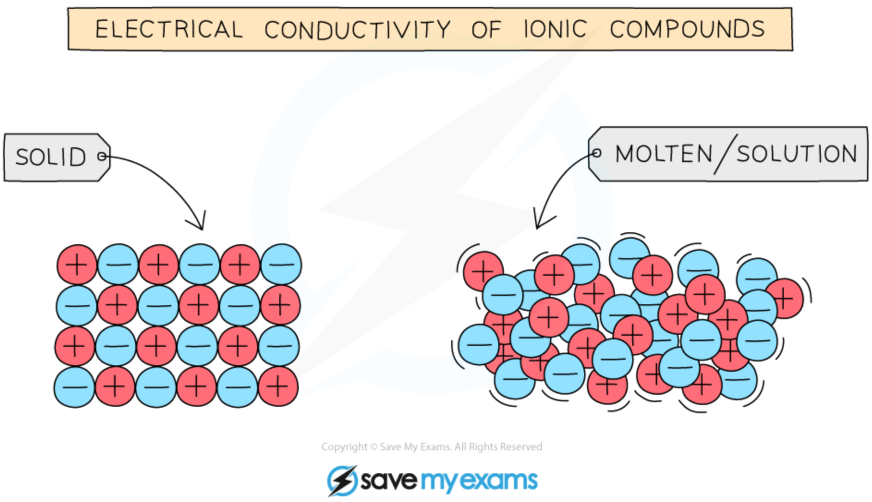
Your notes

Electrolysis

Contents

Electrolysis: general principles

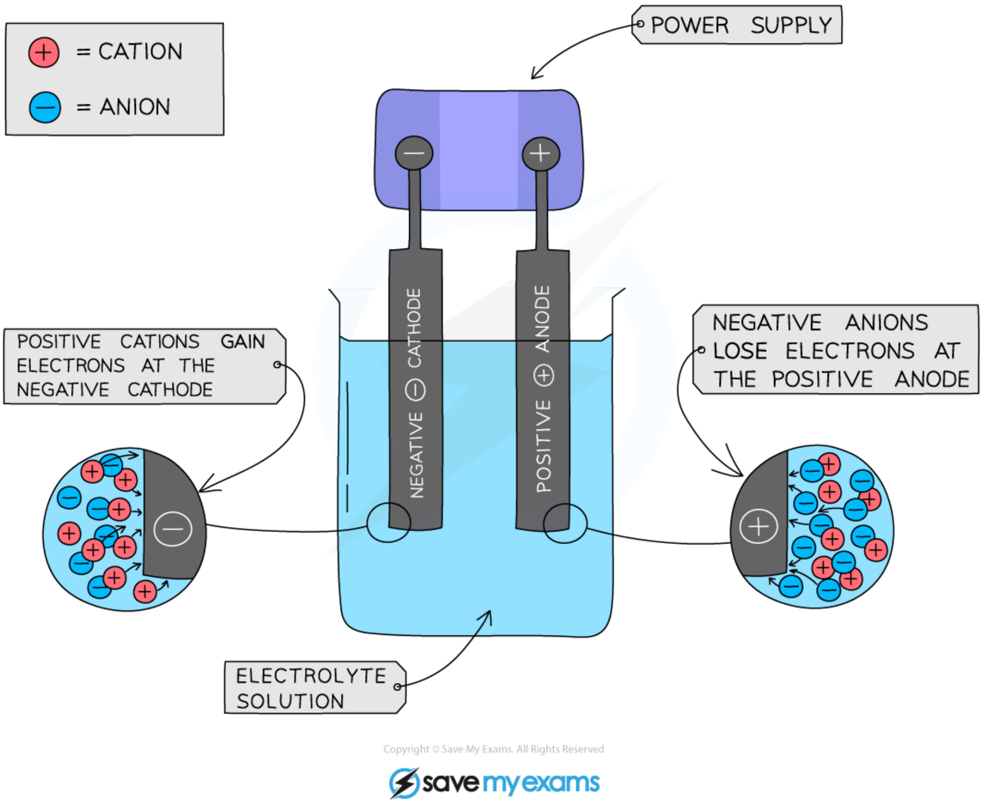
- Electrolysis is the process in which a molten ionic compound is broken down by an electric current
- The process also occurs for **aqueous solutions** of ionic compounds
- Covalent compounds do not conduct electricity, so they cannot undergo electrolysis
- Ionic compounds in the solid state cannot conduct electricity either since they have **no free ions** that can move and carry the charge



In solids, ions are fixed in place. When molten or in solution, they are free to move and carry charge.

Key terms used in a simple electrolytic cell

- **Electrode** is a rod (usually metal or graphite) that conducts electricity into or out of an electrolyte
- **Electrolyte** is the ionic compound in a molten or dissolved solution that conducts the electricity
- **Anode** is the positive electrode of an electrolysis cell
- **Anion** is a negatively charged ion which is attracted to the anode
- **Cathode** is the negative electrode of an electrolysis cell
- **Cation** is a positively charged ion which is attracted to the cathode



The basic set-up of an electrolytic cell

- Metals and hydrogen form positive ions, so a **metal** or **hydrogen** gas is formed at the **cathode**
    - The production of a metal or hydrogen gas depends on the reactivity series
    - If the metal is **less reactive** than hydrogen (e.g. copper, silver), then the **metal** is produced
    - If the metal is **more reactive** than hydrogen (e.g. sodium, magnesium), then **hydrogen** gas is produced instead
- Non-metals form negative ions, so **non-metals (except hydrogen)** are formed at the **anode**

Examiner Tips and Tricks

Use the PANIC mnemonic to remember which electrode is the positive and which is the negative:

Positive (is) Anode Negative Is Cathode

Electrolysis: charge transfer

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Extended tier only

How charge flows in electrolysis

- During electrolysis, current flows around the circuit as **electrons and ions move**
  - **Electrons and ions transfer charge because they are the charged particles**
- Electrons flow from the **negative terminal** of the power supply to the **cathode**
  - This gives the cathode its **negative charge**
- The electrons do not pass through the solution
- At the cathode, cations gain electrons to form atoms
- Meanwhile, **anions** move to the **anode** and lose electrons
  - These electrons then flow through the external circuit back to the power supply's **positive terminal**, completing the circuit
- So, in a complete circuit:
  - **Electrons** are the charge carriers in the **external circuit**
  - **Ions** are the charge carriers in the **electrolyte**

Examiner Tips and Tricks

In electrolysis, we focus on the movement of **electrons**, not the direction of conventional current:

- **Electrons** flow from the **negative terminal to the positive terminal**
- **Conventional current** flows from **positive to negative**

Movement of ions in the electrolyte

- **Positive ions** (cations) in the electrolyte move towards the **cathode**
  - **Reduction** occurs at the **cathode** (gain of electrons)
- **Negative ions** (anions) in the electrolyte move towards the **anode**
  - **Oxidation** occurs at the **anode** (loss of electrons)

Example: sodium chloride electrolysis

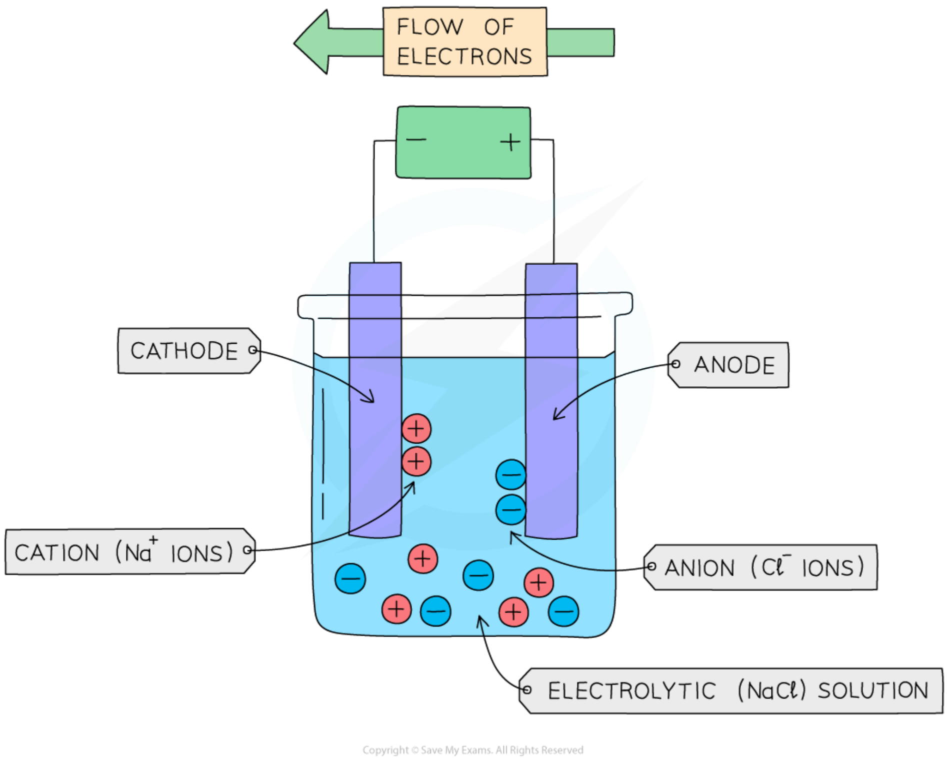


Diagram showing the direction of movement of electrons and ions in the electrolysis of NaCl

- Sodium ions (**Na^+**, cations) move towards the **cathode**
  - The sodium ions gain electrons and are reduced to sodium atoms:

$$\mathbf{Na^+ (aq) + e^- \rightarrow Na (s)}$$

- Chloride ions (**Cl^-**, anions) move towards the **anode**
  - The chloride ions lose electrons and are oxidised to form chlorine gas

$$\mathbf{2Cl^- (aq) \rightarrow Cl_2 (g) + 2e^-}$$

Electrons flow around the external circuit from the power supply's **negative terminal** to the **cathode**

Electrolysis of molten compounds

- A binary ionic compound is one consisting of just two elements joined together by ionic bonding
- When these compounds undergo electrolysis they always produce their corresponding elements
- To predict the products made at each electrode, first identify the ions
- The **positive** ion will migrate towards the **cathode** and the **negative** ion will migrate towards the **anode**
- Therefore, the **cathode** product will always be the **metal,** and the product formed at the **anode** will always be the **non-metal**

Electrolysis of molten lead(II) bromide

Method:

- Add lead(II) bromide into a beaker and heat it so it will turn molten, allowing ions to be free to move and conduct an electric charge
- Add two graphite rods as the electrodes and connect this to a power pack or battery
- Turn on the power pack or battery and allow electrolysis to take place
- Negative bromide ions move to the positive electrode (anode) and each loses one electron to form bromine molecules. There is bubbling at the anode as brown **bromine gas is given off**
- Positive lead ions move to the negative electrode (cathode) and gain electrons to form a **grey lead metal** which deposits on the surface of the electrode

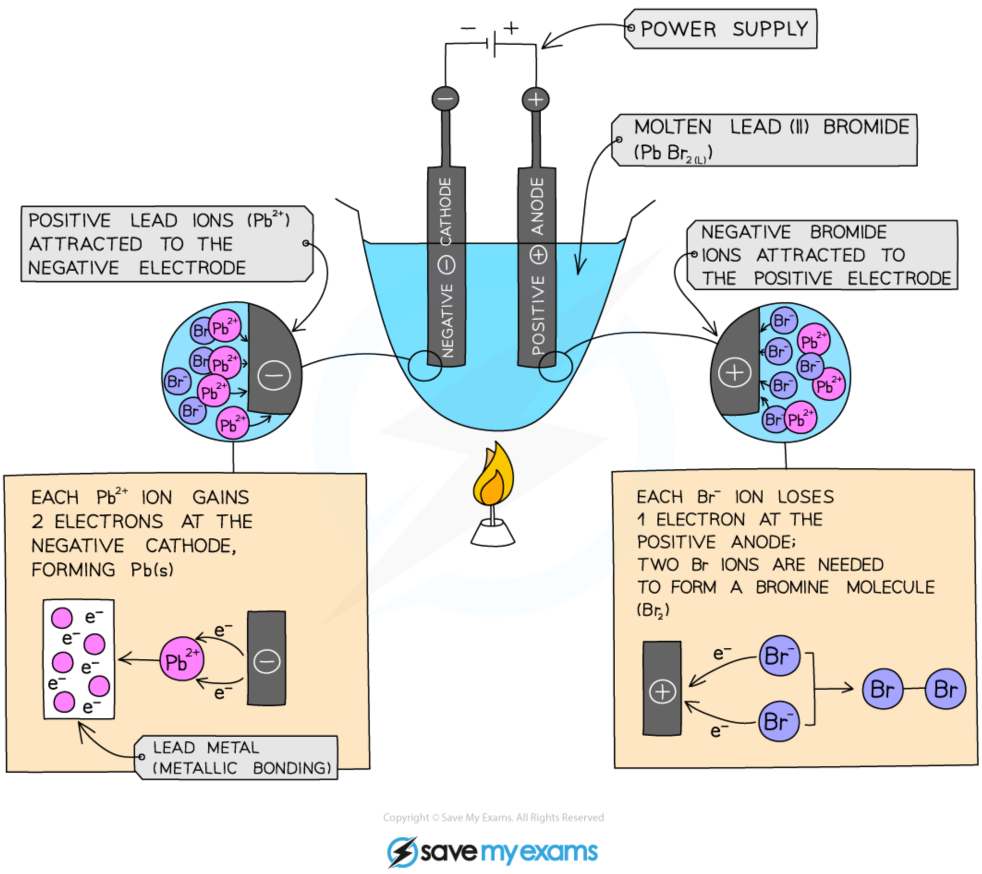


Diagram showing the electrolysis of lead(II) bromide

Worked Example

Identify the product formed at the anode and cathode during the electrolysis of molten potassium chloride.

Answer:

- The ions present are potassium (K^+) and chloride (Cl^-)
- The chloride ions are attracted to the anode and form chlorine gas
- The potassium ions are attracted to the cathode and form potassium metal

Examiner Tips and Tricks

Remember: Electrodes need to be inert such as graphite or platinum so that they don't participate in a side reaction with the electrolyte.

Electrolysis of aqueous sodium chloride & dilute sulfuric acid

Electrolysis of aqueous sodium chloride

- **Brine** is a concentrated solution of aqueous sodium chloride
- It can be electrolysed using inert electrodes made from platinum or carbon / graphite
- The ions in brine are:
  - Na^+ and Cl^- ions from the brine / aqueous sodium chloride
  - H^+ and OH^- ions from the water
- When electrolysed, it produces bubbles of gas at both electrodes
  - The gases chlorine and hydrogen are produced
  - Sodium hydroxide solution is the product remaining in the electrolysis chamber / container
- These substances all have important industrial uses:
  - Chlorine is used to make bleach
  - Hydrogen is used to make margarine
  - Sodium hydroxide is used to make soap and detergents

Product at the negative electrode:

- The H^+ ions are discharged at the **cathode** as they are less reactive than sodium ions
- The H^+ ions gain electrons to form **hydrogen** gas

Product at the positive electrode:

- The Cl^- ions are discharged at the **anode**
- They lose electrons and **chlorine gas forms**
- The Na^+ and OH^- ions remain behind and form the NaOH solution

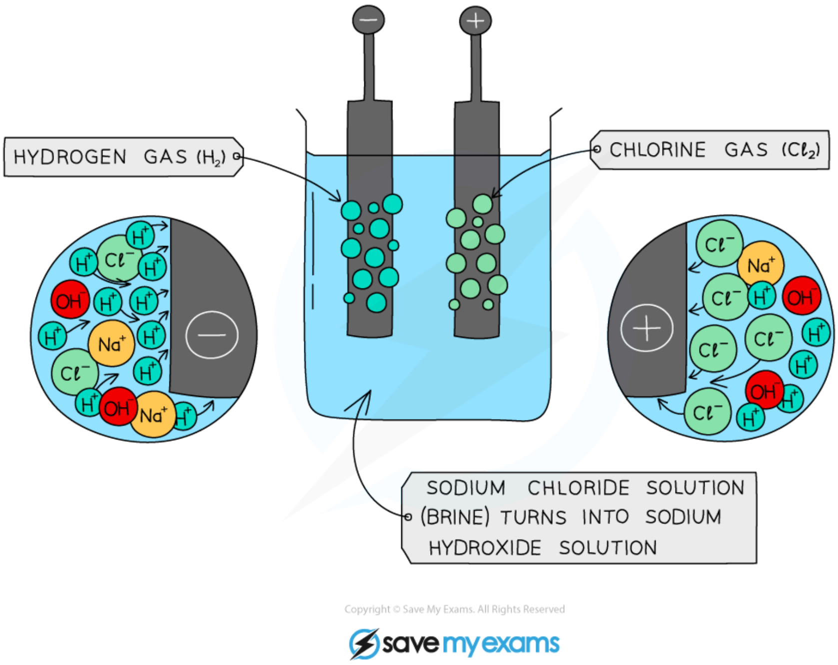
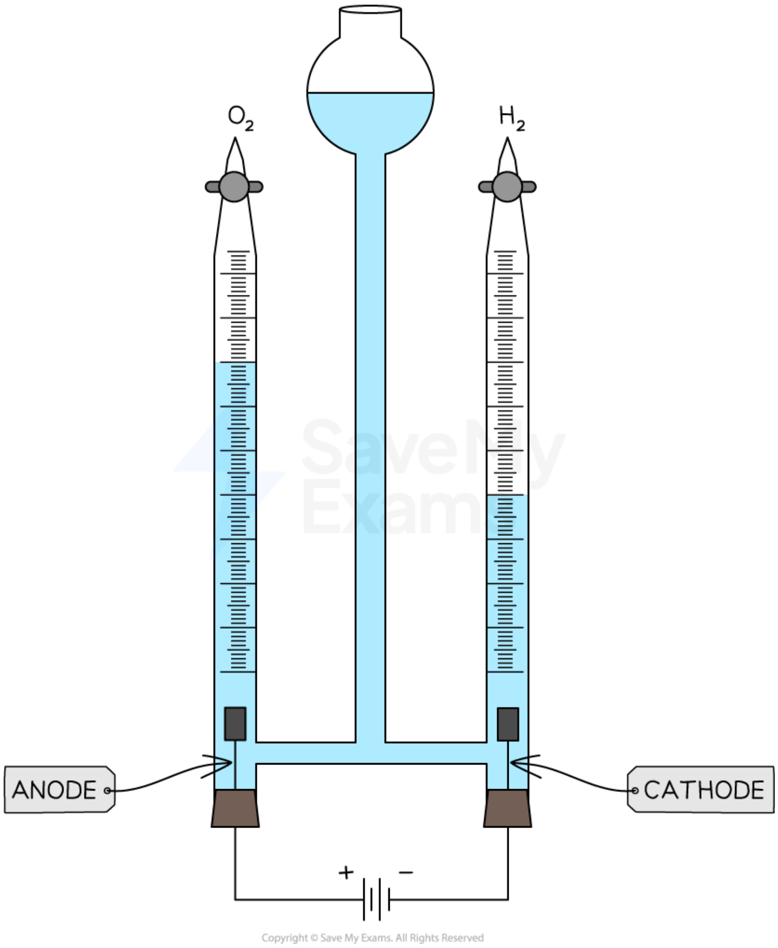


Diagram showing the products of the electrolysis of aqueous sodium chloride

Electrolysis of dilute sulfuric acid

- Dilute sulfuric acid can be electrolysed using inert electrodes made from platinum or carbon / graphite
- The ions in dilute sulfuric acid are:
  - H^+ and SO_4^{2-} ions from the sufuric acid
  - H^+ and OH^- ions from the water
- When electrolysed, it produces bubbles of gas at both electrodes
  - The gases oxygen and hydrogen are produced



Electrolysing dilute sulfuric acid in a Hoffman voltameter shows that twice as much hydrogen is produced, compared to oxygen

Product at the negative electrode:

- H^+ ions are attracted to the **cathode**
- The H^+ ions gain electrons to form **hydrogen** gas

Product at the positive electrode:

- OH^- ions are attracted to the **anode**
- They lose electrons and form **oxygen gas** and water

Examiner Tips and Tricks

- When a gas is produced during electrolysis, you should be able to give the appropriate gas test:

Your notes

- Oxygen - if a glowing splint is dipped into a sample of the gas, then the splint will relight
- Hydrogen - if a lit splint is dipped into a sample of the gas, then a squeaky pop will be heard
- Chlorine - if damp litmus paper is dipped into a sample of the gas, it will turn red and then bleach to a white colour

Your notes

Electrolysis of aqueous solutions

Extended tier only

- Aqueous solutions always have water, H_2O, present
- In the electrolysis of aqueous solutions, the water molecules dissociate producing H^+ and OH^- ions:

$$H_2O \rightleftharpoons H^+ + OH^-$$

- These ions are also involved in the process and their chemistry must be considered
- We now have an electrolyte that contains ions from the compound plus ions from the water
- Which ions get discharged and at which electrode depends on the **relative reactivity** of the elements involved
- Concentrated and dilute solutions of the **same** compound give **different** products
- For anions, the **more concentrated** ion will tend to get discharged over a more dilute ion

Positive electrode – anode

- Negatively charged OH^- ions and non-metal ions are attracted to the positive electrode
- If halide ions (Cl^-, Br^-, I^-) are present, the halogen is produced at the anode
  - The halide ions lose electrons and forms the halogen (chlorine, bromine or iodine)
- If there are no halide ions but OH^- ions are present, oxygen is produced at the anode
  - The hydroxide ions lose electrons and forms oxygen gas (and water)
- In both cases, the other negative ion remains in solution

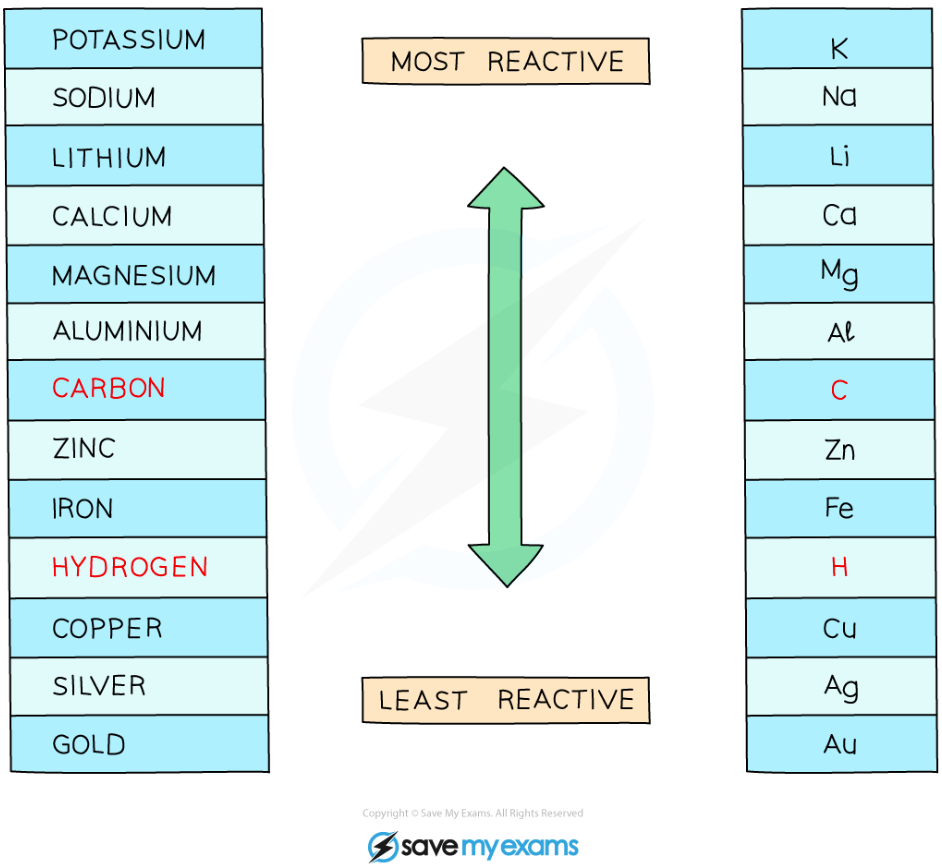
How concentration affects products at the anode

- The concentration of the solution affects the ion being discharged:
  - If a **concentrated** halide solution is being electrolysed, the **halogen** forms at the anode
  - If a **dilute** halide solution is being electrolysed, **oxygen** forms at the anode
- For example:
  - For concentrated barium chloride solution :
    - Cl^- ions are discharged more readily than the OH^- ions
    - So, chlorine gas is produced at the anode
  - For dilute barium chloride solution:

- Only OH^- ions are discharged
- So, oxygen is produced at the anode

Negative electrode – cathode

- Positively charged H^+ and metal ions are attracted to the negative electrode but only one will gain electrons
- Either hydrogen gas or metal will be produced
- If the metal is **above hydrogen** in the reactivity series:
  - The ions of the more reactive metal remain in solution
  - This causes the less reactive hydrogen ions, H^+, to be discharged
  - So, hydrogen will be produced and bubbling will be seen at the cathode
- If the metal is **below hydrogen** in the reactivity series:
  - The less reactive metal ions are discharged
  - So, the **metal** is produced and this will be seen plating onto the cathode



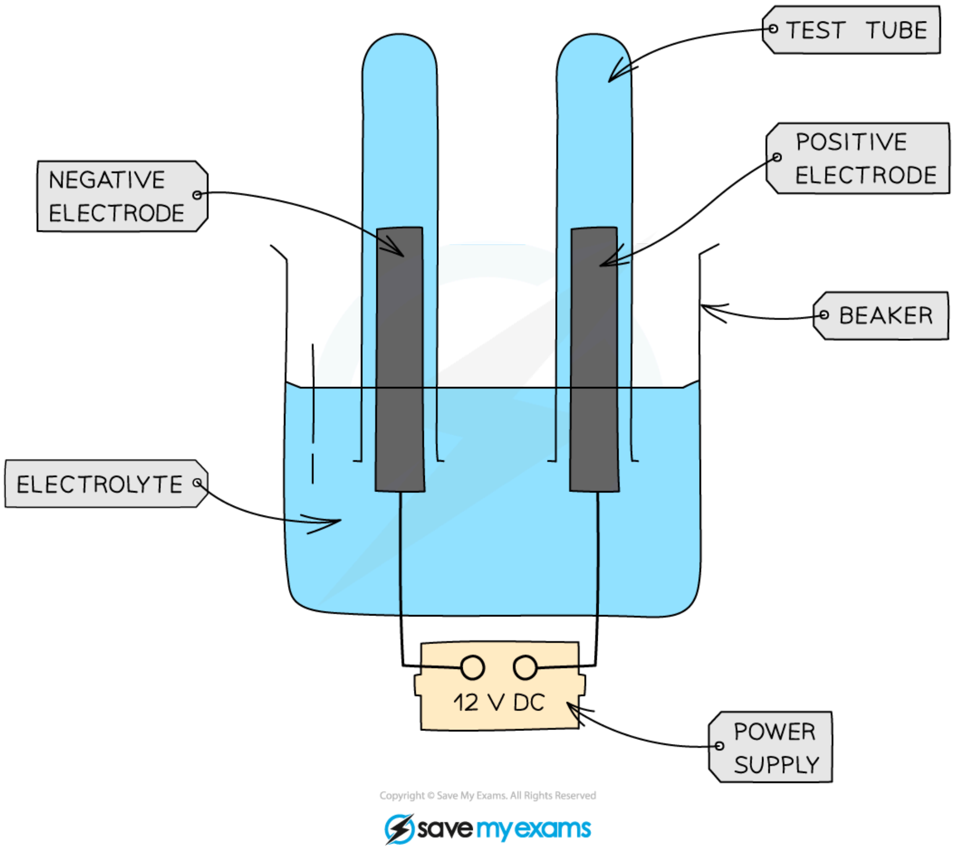
The reactivity series of metals including hydrogen and carbon

Electrolysis of aqueous copper sulfate

Your notes

- Aqueous copper sulfate contains the following ions:
  - Cu^{2+} and SO_4^{2-} from the copper sulfate
  - H^+ and OH^- from the water

Using graphite electrodes:



Apparatus for the electrolysis of copper(II)sulfate using inert / passive graphite electrodes

Observations:

- The cathode is coated with a **pink-brown layer** of copper metal
- Bubbles of a **colourless gas** (oxygen) are seen forming at the anode
- The **blue colour** of the copper(II) sulfate solution **fades** over time

Product at the cathode:

- Cu^{2+} and H^+ will both be attracted to the cathode but the less reactive ion will be discharged
  - In this case, copper is less reactive than hydrogen
  - Copper ions are discharged at the cathode

Your notes

- They gain electrons and are reduced to form copper metal
- The half equation for the reaction at the electrode is:

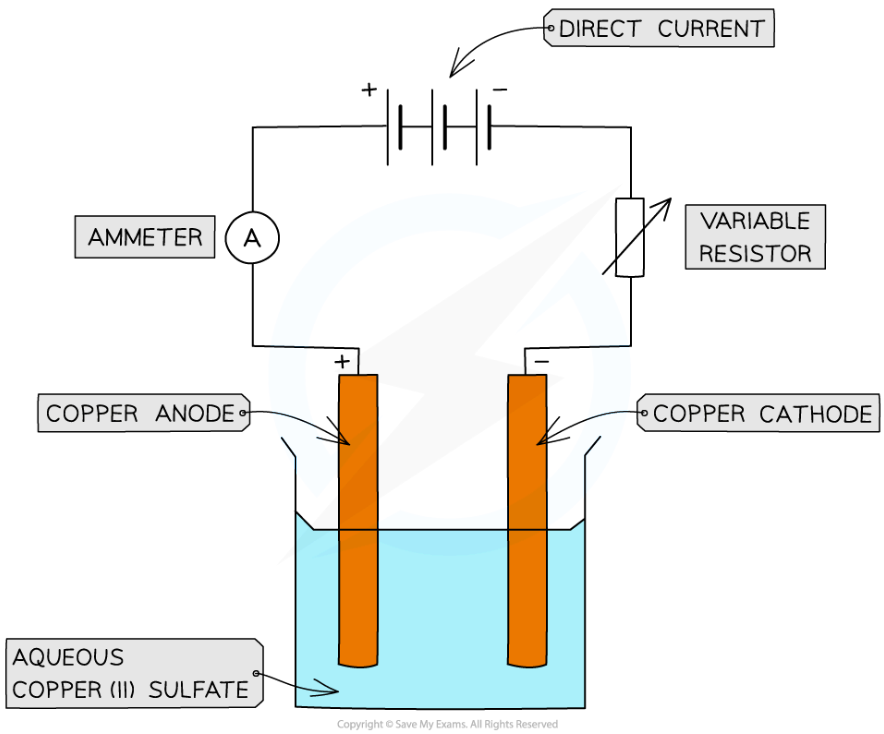
$$Cu^{2+} + 2e^- \rightarrow Cu$$

Product at the anode:

- SO_4^{2-} and OH^- are both attracted to the anode
  - OH^- ions lose electrons more readily than SO_4^{2-}
  - OH^- lose electrons and are oxidised to form oxygen gas
  - The half equation for the reaction at the anode is

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$$

Using copper electrodes:



Apparatus for the electrolysis of copper(II)sulfate using active copper electrodes

Observations at the anode and cathode:

- The **blue colour** of the copper(II) sulfate solution **remains unchanged**
- The **cathode increases** in mass as it is coated with a layer of copper
  - This is because copper ions, Cu^{2+}, are **reduced** at the cathode and form copper atoms
- The **anode decreases** in mass as it dissolves
  - This is because copper atoms are **oxidised** at the anode and form copper ions, Cu^{2+}

Your notes

- The gain in mass by the negative electrode is the **same** as the loss in mass by the positive electrode
  - Therefore, the copper deposited on the negative electrode must be the **same** copper ions that are lost from the positive electrode
- This implies that the concentration of the Cu^{2+} ions in the solution remains **constant**

Products formed for common aqueous solutions

Aqueous solution – ions present	**Product at the anode**	**Product at the cathode**
Concentrated sodium chloride, NaCl	Chlorine gas	Hydrogen gas
Dilute sodium chloride, NaCl	Oxygen gas	Hydrogen gas
Concentrated aqueous copper(II) sulfate, $CuSO_4$	Oxygen gas	Copper
Dilute sulfuric acid, H_2SO_4	Oxygen gas	Hydrogen gas

Your notes

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Ionic half equations

Extended tier only

- Electrochemistry is concerned with the transfer of electrons
  - This is why the definitions of oxidation and reduction are in terms of losing or gaining electrons, not oxygen
  - **Oxidation** is the **loss of electrons**
  - **Reduction** is the **gain of electrons**
- As the ions come into contact with the electrode:
  - Electrons are lost or gained
  - The ions form **neutral s**ubstances
  - These substances are discharged as products at the electrodes
- At the **anode**, negatively charged ions **lose electrons**
  - So, oxidation occurs at the anode
- At the **cathode,** the positively charged ions **gain electrons**
  - So, reduction occurs at the cathode
- **Ionic half-equations** only show **half** of what is happening in a reaction involving electron transfer
  - The ionic half-equation for oxidation shows the loss of electrons
  - The ionic half-equation for reduction shows the gain of electrons
- Ionic half-equations must have the atoms and charges balanced

Writing ionic half-equations

Metals

- Metals are positive ions, e.g. Li^+, Cu^{2+}, Al^{3+}
- If a metal is produced during electrolysis:
  - The metal ions will gain electrons to form metal atoms
  - The metal ions will be reduced
- The charge on the metal ion indicates the number of electrons that will be gained
  - For example:

$$\mathbf{Li^+ + e^- \rightarrow Li}$$

$$Cu^{2+} + 2e^- \rightarrow Cu$$

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

Non-metals

- Non-metals are typically negative ions, e.g. Cl^-, Br^-, OH^-
  - The hydrogen ion, H^+, is an exception to this

Hydrogen ion / hydrogen half-equation:

- If hydrogen is formed during electrolysis:
  - **Two** hydrogen ions will **gain** 2 electrons to form hydrogen, H_2
  - Hydrogen ions are **reduced**

$$2H^+ + 2e^- \rightarrow H_2$$

Halide ion / halogen half-equation:

- If a halogen is formed during electrolysis:
  - **Two** halide ions will **lose** 2 electrons to form the halogen
  - Halide ions are **oxidised**

$$2X^- \rightarrow X_2 + 2e^-$$

Hydroxide ion / oxygen half-equation:

- The ionic half-equation for hydroixde ions forming oxygen is more challenging to balance
  - Hydroxide ions **lose** electrons to form oxygen, O_2, and water, H_2O
  - Hydroxide ions are **oxidised**

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$$

Table of reduction and oxidation reactions at the electrodes

Electrolysis of	Anode reaction	Cathode reaction
Molten lead(II) bromide, $PbBr_2$	$2Br^- \rightarrow Br_2 + 2e^-$	$Pb^{2+} + 2e^- \rightarrow Pb$
Concentrated aqueous sodium chloride, NaCl	$2Cl^- \rightarrow Cl_2 + 2e^-$	$2H^+ + 2e^- \rightarrow H_2$
Dilute sulfuric acid, H_2SO_4	$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$	$2H^+ + 2e^- \rightarrow H_2$

Your notes

Your notes

Examiner Tips and Tricks

- To help you remember the definitions of oxidation and reduction, use OIL RIG
    - **O**xidation **I**s **L**oss (of electrons) **R**eduction **I**s **G**ain (of electrons)
- To help you remember where oxidation and reduction take place, use a RED CAT and AN OX
    - **RED**uction at the **CAT**hode
    - **AN**ode for **OX**idation