



Electrolysis

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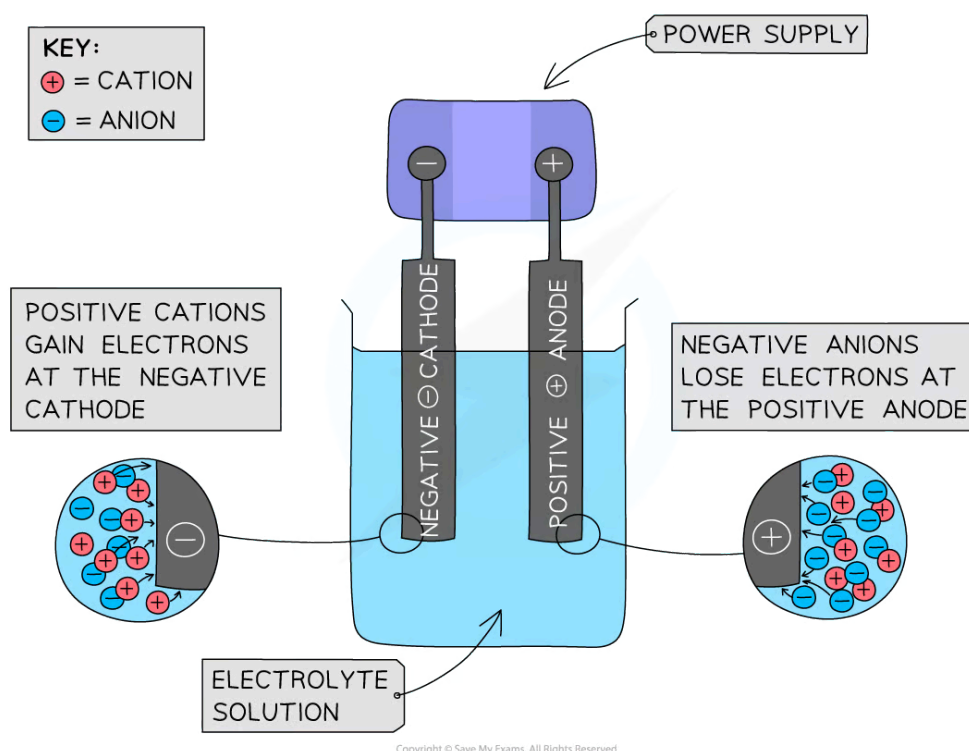
Electrolytic cells

- When an electric current is passed through a **molten ionic compound** the compound **decomposes** or breaks down
- The process also occurs for **aqueous solutions** of ionic compounds
- Liquids and solutions that are able to conduct electricity are called **electrolytes**
- Covalent compounds **cannot conduct electricity** hence they do not undergo electrolysis
- An electrolytic cell is the name given to the set-up used in electrolysis and which consists of the following:
 - **Electrode:** a rod of metal or graphite through which an electric current flows into or out of an electrolyte
 - **Electrolyte:** ionic compound in molten or dissolved solution that conducts the electricity
 - **Anode:** the positive electrode of an electrolysis cell
 - **Anion:** negatively charged ion which is attracted to the anode
 - **Cathode:** the negative electrode of an electrolysis cell
 - **Cation:** positively charged ion which is attracted to the cathode

An electrolytic cell



Your notes



The basic set-up of an electrolysis cell



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.

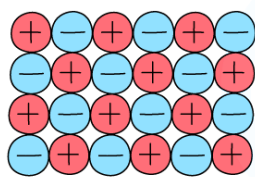
Electrical conductivity of ionic compounds

Electrical Conductivity of Ionic Compounds

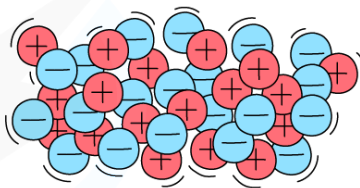
- Ionic compounds in the solid state **cannot** conduct electricity since they have no free ions that can move and carry the charge
- The ions must be able to move and can only do so in the molten state or when dissolved in a solution, usually aqueous
- When the cell is turned on and an electric current is passed through an electrolyte the ions in the solution start to move towards the electrodes

Particles in solid and molten / solution in ionic compounds

ELECTRICAL CONDUCTIVITY OF IONIC COMPOUNDS



SOLID



MOLTEN / SOLUTION

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Your notes

Particles in ionic compounds are in fixed position in the solid state but can move around when molten or in solution



Examiner Tips and Tricks

Cations are attracted to the cathode and anions are attracted to the anode. Electron flow in electrochemistry occurs in alphabetical order as electrons flow from the anode to the cathode.

Movement of ions

Movement of ions during electrolysis

- During electrolysis the electrons move from the power supply towards the **cathode**
- Electron flow in electrochemistry thus occurs in **alphabetical** order as electrons flow from the **anode** to the **cathode**
- Positive ions within the electrolyte migrate towards the **negatively** charged electrode which is the **cathode**
- Negative ions within the electrolyte migrate towards the **positively** charged electrode which is the **anode**

The flow of electrons and ions in electrolysis

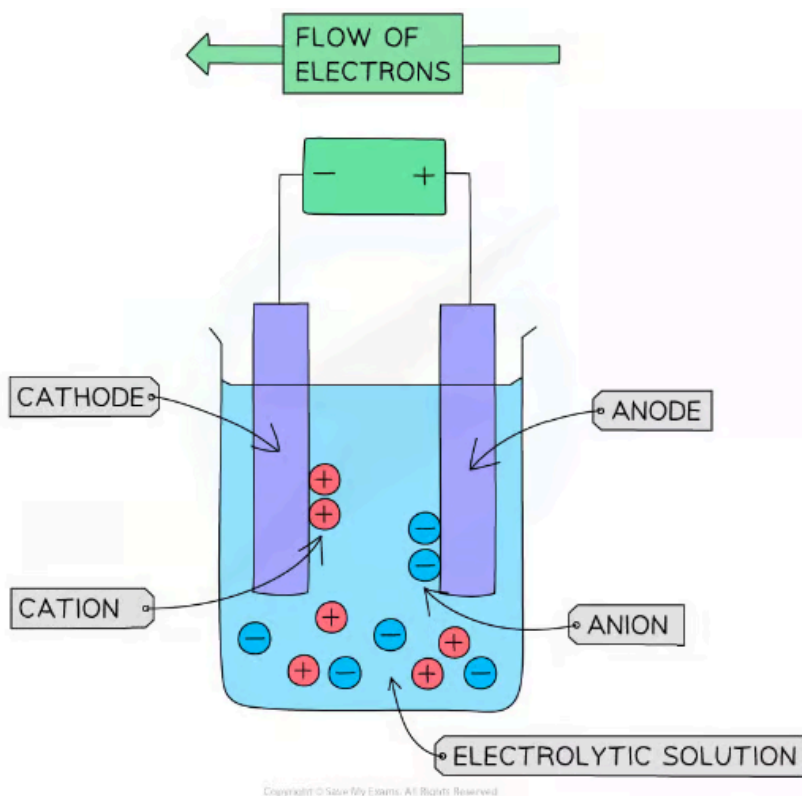


Diagram showing the direction of movement of electrons and ions in the electrolysis of NaCl



Examiner Tips and Tricks

When a metal conducts it is the **electrons** that are moving through the metal. When a salt solution conducts it is the **ions** in the solution that move towards the electrodes while carrying the electrons.

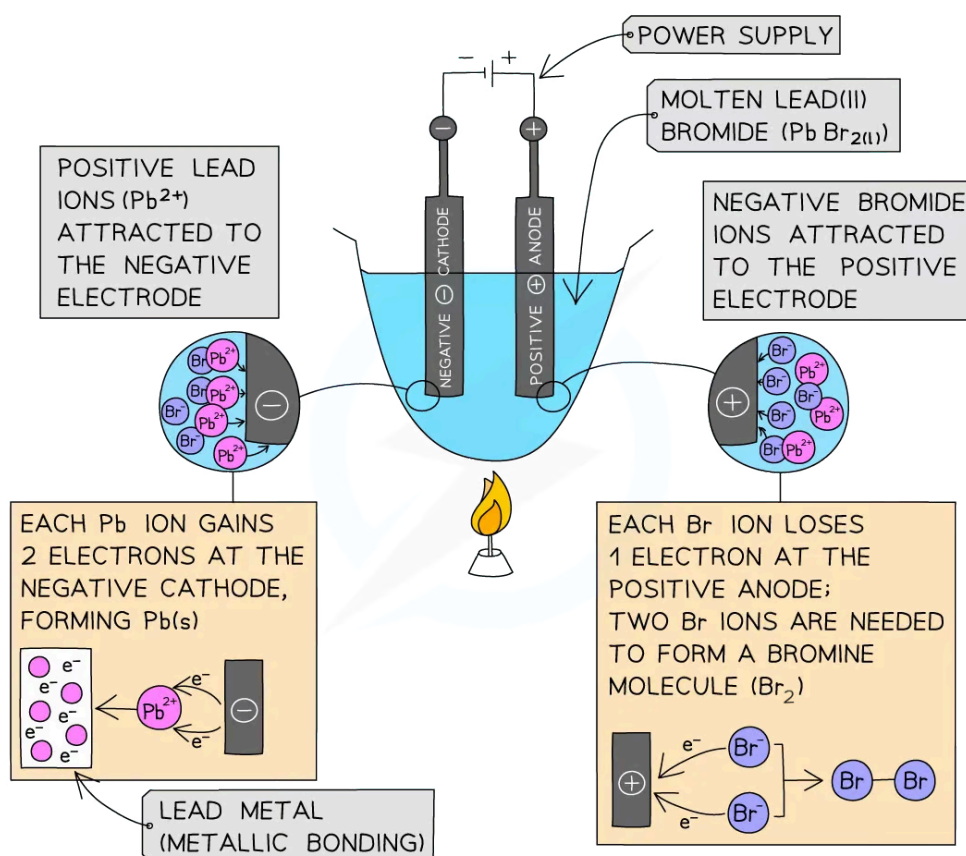


Electrolysis of simple ionic compounds

What is produced at the anode and cathode?

- Lead(II) bromide is a binary **ionic compound** meaning that it is a compound consisting of just two elements joined together by ionic bonding
- When these compounds are heated beyond their melting point, they become molten and can conduct electricity as their ions can move freely and carry the charge
- These compounds undergo electrolysis and always produce their corresponding element
- To predict the products of any binary molten compound first identify the ions present
- 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



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Method

- Add lead(II) bromide into a crucible and heat 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 lose two electrons 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 grey lead metal which deposits on the bottom of the electrode

What are the products at the anode and cathode?

- **Anode:** Bromine gas
- **Cathode:** Lead 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.



Extracting metals

Choosing methods for metal extraction

- The position of the metal on the reactivity series determines the method of extraction
- Higher placed metals (above carbon) have to be extracted using **electrolysis** as they are too reactive and cannot be reduced by carbon
- Lower placed metals can be extracted by heating with carbon which **reduces**
- Electrolysis is very expensive as **large amounts of energy** are required to melt the ores and produce the electrical current
- The reactivity series of metals is shown below with the corresponding method of extraction

Extracting metals

Metal	Extraction method
Most reactive	
Potassium	Extracted by electrolysis of the molten chloride or oxide Large amounts of electricity are required, which makes this an expensive process
Sodium	
Lithium	
Calcium	
Magnesium	
Aluminium	
Zinc	Extracted by heating with a reducing agent such as carbon or carbon monoxide in a blast furnace A cheap process as carbon is cheap and can also be a source of heat
Iron	
Copper	
Silver	Found as pure elements
Gold	



Examiner Tips and Tricks

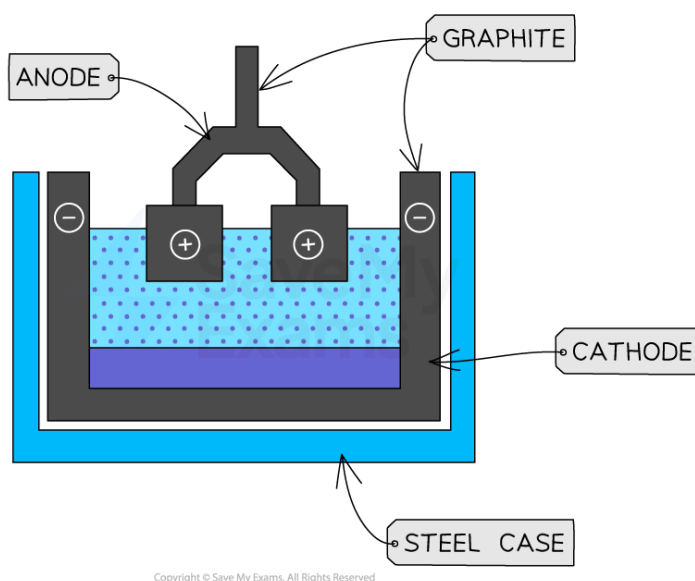
Questions on this topic often ask you to explain why in some cases electrolysis is used and in other cases reduction by heating with carbon is used. Make sure you can explain when each process is used and why.

The extraction of aluminium

How is aluminium extracted?

- Aluminium is a reactive metal, above carbon in the reactivity series
- Its main ore, is **bauxite**, which contains aluminium oxide
- Aluminium is higher in the reactivity series than carbon, so it cannot be extracted by reduction using carbon
- Instead, aluminium is extracted by **electrolysis**

The electrolytic cell for extraction of aluminium



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Diagram showing the extraction of aluminium by electrolysis

- Bauxite is first **purified** to produce aluminium oxide, Al_2O_3
- Aluminium oxide is then dissolved in **molten cryolite**
 - This is because aluminium oxide has a melting point of over 2000°C which would use a lot of energy and be very expensive

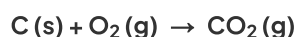


Your notes

- The resulting mixture has a lower melting point without interfering with the reaction
- The mixture is placed in an electrolysis cell, made from steel, lined with graphite
- The **graphite** lining acts as the negative electrode, with several large graphite blocks as the positive electrodes
- Aluminium is produced at the cathode
- Oxygen is produced At the **anode**

Why does the anode need to be replaced?

- The carbon in the **graphite** anodes reacts with the oxygen produced to produce CO_2



- As a result the anode wears away and has to be replaced regularly
- A lot of **electricity** is required for this process of extraction, this is a major **expense**



Examiner Tips and Tricks

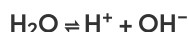
Questions on this topic often ask you to explain why cryolite is used in the process so make sure you are able to explain its use, providing reasons for your answer.



Electrolysis of an aqueous solution using inert electrodes

Ions present in aqueous solutions

- Aqueous solutions will always contain water molecules (H_2O)
- In the electrolysis of aqueous solutions, the water molecules dissociate producing H^+ and OH^- ions:



- These ions are also involved in the electrolysis 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

Note: The concentration of the solution can affect the products of electrolysis, however, this is beyond the scope of this course and you are not expected to know the specific details of this



Examiner Tips and Tricks

When answering questions on this topic, it helps if you first write down all of the ions present first. Only then you should start comparing their reactivity and deducing the products formed.

Electrode reactions

What is produced at the positive electrode?

- Negatively charged OH^- ions and non-metal ions are attracted to the positive electrode
- If halide ions (Cl^- , Br^- , I^-) and OH^- are present then the halide ion is discharged at the anode, loses electrons and forms a halogen (chlorine, bromine or iodine)
- If no halide ions are present, then OH^- is discharged at the anode, loses electrons and forms oxygen
- In both cases the other negative ion remains in solution

What is produced at the 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 the metal will be produced
- If the metal is **above hydrogen** in the reactivity series, then hydrogen will be produced and bubbling will be seen at the cathode
- This is because the more reactive ions will remain in solution, causing the least reactive ion to be discharged
- Therefore at the cathode, **hydrogen gas** will be produced unless the positive ions from the ionic compound are less reactive than hydrogen, in which case the **metal** is produced



Your notes

The reactivity series

POTASSIUM	MOST REACTIVE	K
SODIUM		Na
LITHIUM		Li
CALCIUM		Ca
MAGNESIUM		Mg
ALUMINIUM		Al
CARBON		C
ZINC		Zn
IRON		Fe
HYDROGEN		H
COPPER		Cu
SILVER		Ag
GOLD	LEAST REACTIVE	Au

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The reactivity series of metals including hydrogen and carbon



Worked Example

Predict the products formed at each electrode in the electrolysis of magnesium iodide solution.



Your notes

Answer

1. Work out what ions are attracted to the cathode

- **Hydrogen (H^+) and magnesium (Mg^{2+})**

2. Decide which element will be discharged:

- The less reactive element is usually formed
- **Hydrogen is discharged at the cathode as it is less reactive than magnesium**

3. Work out what ions are attracted to the anode

- **Hydroxide (OH^-) and iodide (I^-)**

4. Decide which element will be discharged:

- If a halide is present, the corresponding halogen is formed, otherwise, oxygen is formed
- **Iodine is discharged at the anode as iodide ions are present**



Worked Example

Predict the products formed at each electrode in the electrolysis of copper sulfate solution

Answer

1. Work out what ions are attracted to the cathode

- **Hydrogen (H^+) and copper (Cu^{2+})**

2. Decide which element will be discharged:

- The less reactive element is usually formed
- **Copper is discharged at the cathode as it is less reactive than hydrogen**

3. Work out what ions are attracted to the anode

- **Hydroxide (OH^-) and sulfate (SO_4^{2-})**

4. Decide which element will be discharged:

- If a halide is present, the corresponding halogen is formed, otherwise, oxygen is formed
- **Oxygen is discharged at the anode as no halide ions are present**

Determining what gas is produced

- The gas produced can be tested to determine its identity
- If the gas produced at the **cathode** burns with a 'pop' with a lighted splint then the gas is **hydrogen**
- If the gas produced at the **anode** relights a glowing splint dipped into the gas then the gas is **oxygen**
- If the gas produced at the **anode** turns damp blue litmus paper red and is then bleached white then the gas is **chlorine**

- The halogen gases all produce their own colours (bromine is **red-brown**, chlorine is **yellow-green**)



Examiner Tips and Tricks

Once you have identified the ions, the next step is to decide towards which electrode will they be drawn and identify the product formed. It helps if you recall the reactivity series.



Your notes



Required practical 3: Electrolysis of aqueous solutions

Objective

To investigate what happens when aqueous solutions are electrolysed using inert electrodes

Hypothesis

A metal will be produced at the negative electrode because metal ions are positive

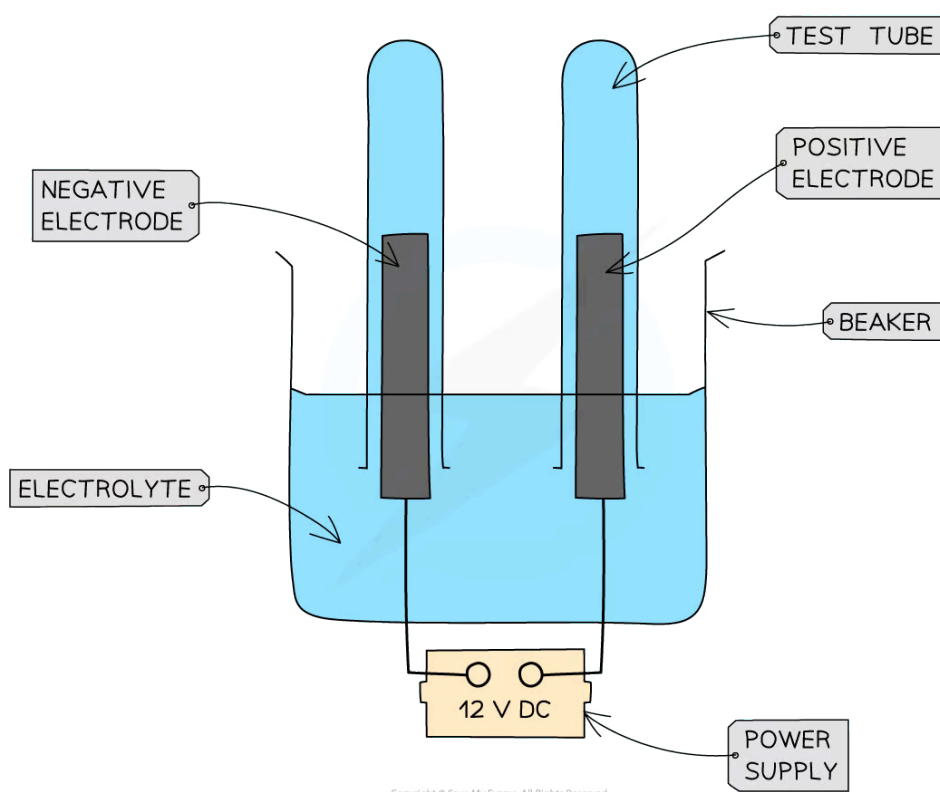
Materials

- Test tubes
- Electrolyte solutions
- 100 cm³ beaker
- Stand and clamp
- Two carbon rod electrodes
- Two crocodile / 4 mm plug leads
- Low voltage power supply
- Blue litmus paper

Electrolytic cell



Your notes



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Diagram showing the electrolysis of aqueous solutions

Practical Tips

1. Make sure the test tubes do not cover the electrodes completely and fall to the bottom of the cell or the conductivity will fall considerably and the rate of electrolysis will be very slow
2. Replacing the test tubes with graduated test tubes or measuring cylinders means that the volume of gas produced over time can be measured

Method

1. Set up the apparatus as shown in the diagram
2. Add the aqueous solution to the beaker
3. Add two graphite rods as the electrodes and connect this to a power pack or battery
4. Turn on the power pack or battery and allow electrolysis to take place
5. Record the results in a suitable table (see below) and repeat for another solution, checking the electrodes in between runs to see if any metal has been deposited
6. The following aqueous solutions are suitable for this investigation: copper chloride, copper sulfate, sodium chloride, sodium bromide, sodium nitrate
7. The gases produced can be collected in the test tubes to be tested later

Results: Record your results in a suitable table:

Electrolysis of aqueous solutions table

Electrolyte	Observations at anode & gas test results	Observation at cathode & gas test result
Aqueous sodium nitrate, NaNO_3	Effervescence, no colour, splint relights so gas is oxygen	Effervescence, no colour, squeaky pop, so gas is hydrogen



Your notes

Evaluation

The gases and corresponding tests are:

- Hydrogen – lighted splint goes out with a squeaky pop
- Oxygen – a glowing splint relights
- Chlorine – damp blue litmus paper turns red and is then bleached white

Conclusion

Describe how the results obtained compare with the expected results based on the hypothesis



Half equations

Higher tier only

- In electrochemistry we are mostly concerned with the **transfer of electrons**, hence the definitions of oxidation and reduction are applied in terms of **electron loss** or **gain** rather than the addition or removal of oxygen
- **Oxidation** is when a substance **loses electrons** and **reduction** is when a substance **gains electrons**
- As the ions come into contact with the electrode, electrons are either lost or gained and they form **neutral** substances
- These are then **discharged** as products at the electrodes
- At the anode, negatively charged ions lose electrons and are thus **oxidised**
- At the cathode, the positively charged ions gain electrons and are thus **reduced**
- This can be illustrated using half equations which describe the movement of electrons at each electrode
- It is important to make sure that the **charges** as well as the number of atoms/ions on each side of the equation are **balanced**

Electrolysis of molten lead(II)bromide

- In the electrolysis of molten lead(II) bromide the half equation at the negative electrode (cathode) is:



- At the positive electrode (anode) bromine gas is produced by the discharge of bromide ions:

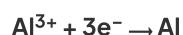


OR



Electrolysis of molten aluminium oxide

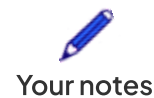
- Aluminium ions are discharged at the negative electrode (cathode) and the aluminium is collected at the bottom of the cell:



- At the positive electrode (anode) oxygen gas is produced:



OR



Electrolysis of aqueous solutions

- At the negative electrode (cathode), when the metal is more reactive than hydrogen, hydrogen is discharged and the half equation is:



- When the metal is less reactive than hydrogen, the metal is discharged, e.g.:



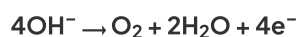
- At the positive electrode (anode), if a halide ion is present, the corresponding halogen is formed e.g.:



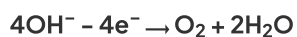
OR



- When a halide ion is not present, oxygen is formed as hydroxide ions are discharged, e.g.:



OR



Summary of the half equations at the anode and cathode

Half equations at electrodes		
Electrolyte	Anode reaction	Cathode reaction
Copper(II) chloride (CuCl_2)	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
Sodium chloride (NaCl)	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
Copper(II) sulfate (CuSO_4)	$4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
Sodium sulfate (Na_2SO_4)	$4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
Concentrated hydrochloric acid (HCl)	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
Water acidified with sulfuric acid (H_2SO_4)	$4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$



Examiner Tips and Tricks

Don't forget to make sure the charges are balanced within the equation!



Your notes