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ELECTROLYSIS

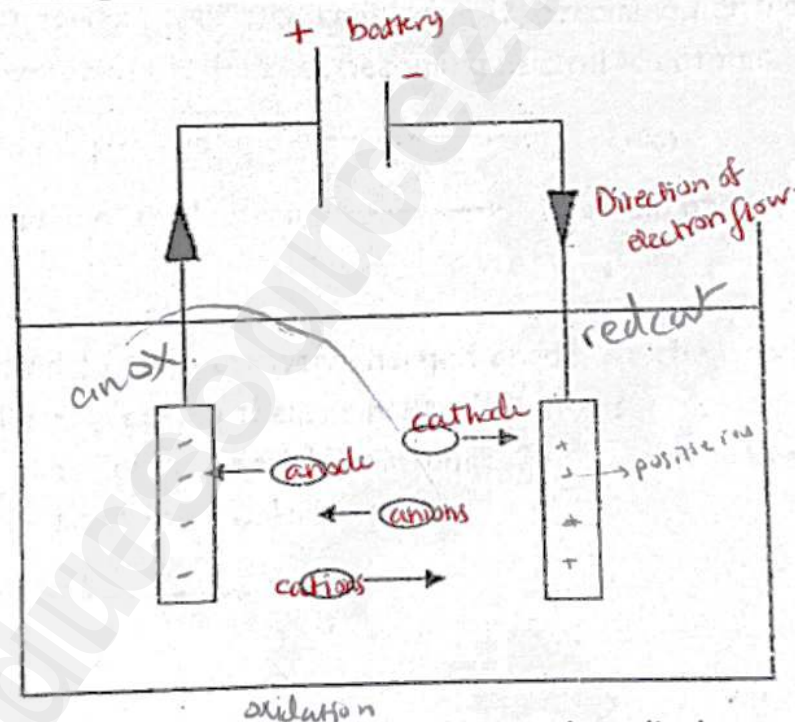
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Electrolysis means using electricity to split up (decompose) substances. The substance that is decomposed is called the electrolyte. Two electrodes are used to make electrical contact with the ^{electrolyte} solution. They are usually made of an unreactive (inert) substance like carbon or platinum. The positive electrode is called the anode and the negative electrode is called the cathode. Electricity is carried through the electrolyte by ions (NOT electrons). The electrolyte must be a substance which will conduct electricity and which is decomposed by it. The common electrolytes are:

- Molten ionic compounds *solid heated → liquid*
 - Aqueous salt solutions *dissolved in water*
 - Acids in aqueous solution
 - Alkalis in aqueous solution
- aqueous ionic solution*

P A N C
 Positive anode
 Negative cathode

What happens during electrolysis?



External circuit is also in the electrolyte.

⊖ anion
 ⊕ cation

Note - Anions release electrons at the anode. As they discharge, these electrons flow through the external circuit to the cathode where they combine with cations in order to discharge them.

- **At the Anode** - Anions move to the anode. When they reach it, they give up electrons becoming *oxidised*. (At the anode, a non-metal (other than hydrogen) is usually formed.)

The electrolyte stays molten because of the huge amount of current.

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- Red Cat anox
- At the Cathode, Cations to the cathode. When they reach it, they pick up electrons becoming *reduced*. (At the cathode, a metal or hydrogen is usually formed.)

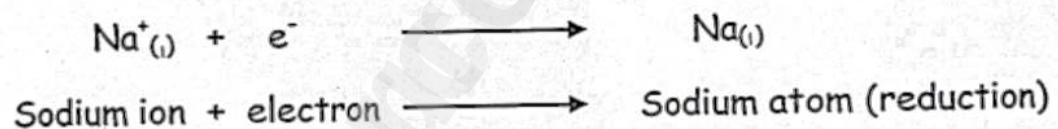
Example - Electrolysis of a molten electrolyte such as molten sodium chloride (NaCl). It is easy to predict the result of electrolysis of a molten electrolyte. The compound just gets split into two parts, a metal and non-metal. The metal is formed at the cathode (-ve), and the non-metal at the anode (+ve). So in this case, Chlorine (gas) is formed at the anode and sodium (metal) at the cathode and nothing is left behind. The electrolyte is used up.

Explanation

At the cathode:

Na^+ ions are attracted to the cathode because it has an excess of electrons - that's why it's negatively charged.

At the cathode, Na^+ ions accept electrons from it, becoming neutral Na atoms. We say the Na^+ ions have been discharged, becoming neutral Na atoms.

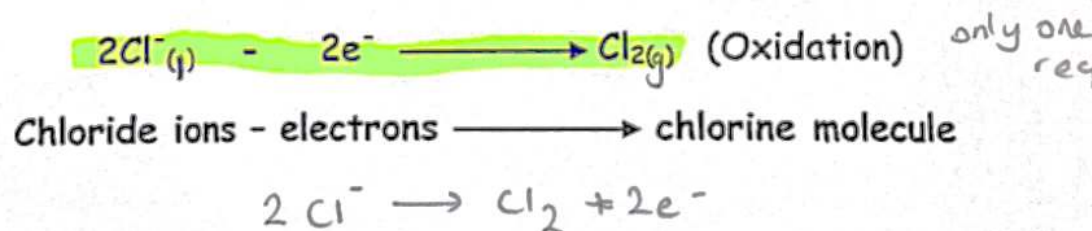


At the anode:

Cl^- ions are attracted to the positively charged anode. At the anode, electrons are taken from the Cl^- ions, leaving them as neutral Cl atoms. Chlorine atoms prefer to go in pairs and so they join up, forming diatomic Cl_2 molecules. We say the Cl^- ions have been discharged and form Chlorine gas.

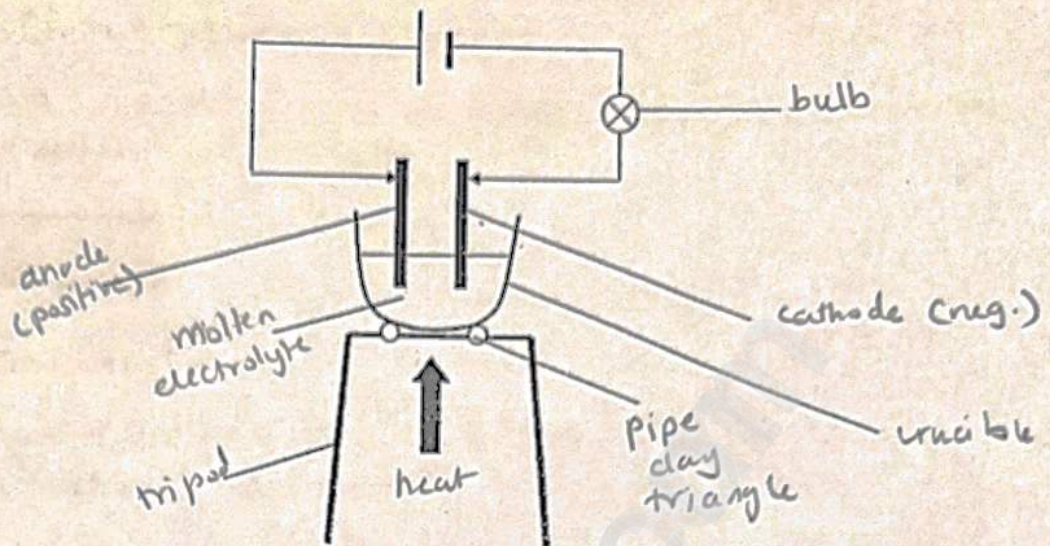
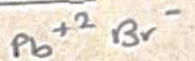


So overall, at the anode,

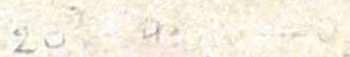
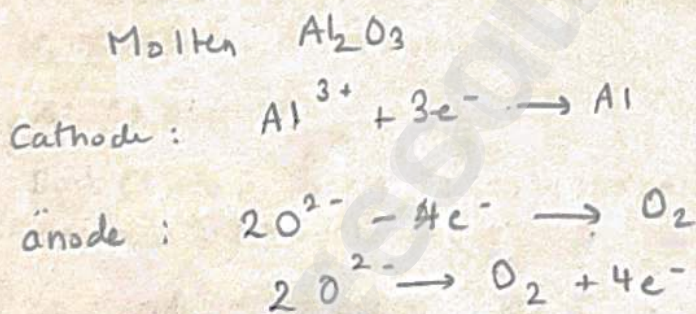
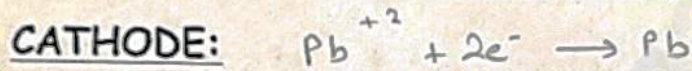


Apparatus for Electrolysis of a molten salt, e.g. Lead(II)Bromide(PbBr₂)

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Label the diagram and write the equations at both electrodes:



Electrolysis of aqueous solutions, e.g. NaCl(aq)

*Chlorine gas is formed at the anode and hydrogen gas at the cathode and a solution of sodium hydroxide is left behind.

Explanation - A solution of sodium chloride contains four different ions: Na^+ and Cl^- , and H^+ and OH^- (from the water).



Water $\longrightarrow$ Hydrogen ions + Hydroxide ions

At the Cathode:

Both Na^+ and H^+ are attracted to the cathode but only the H^+ ions get discharged by gaining electrons and forming Hydrogen gas.



So overall, at the cathode: $2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_{2(\text{g})}$

Na^+ ions remain behind in solution. Note that the least reactive element is always discharged. Hydrogen is less reactive than all metals except copper, silver, gold and platinum. (H_2 is always discharged in preference to a metal unless it is one of the above.) EXCEPTION IS ZINC.

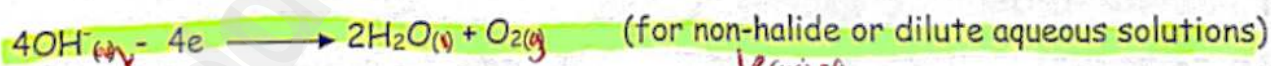
(The more reactive element has a stronger tendency to exist as ions and thus remains behind in the solution.)

At the Anode:

Both Cl^- and OH^- are attracted to the anode but only Cl^- gets discharged by losing electrons to form chlorine gas*. *Potentially* *As long as it's concentrated.*

So overall, at the anode: $2\text{Cl}^-(\text{aq}) - 2\text{e}^- \longrightarrow \text{Cl}_{2(\text{g})}$

OH^- ions are left behind in solution. Note that Halide ions (F^- , Cl^- , Br^- , I^-) are always discharged to make the gas, otherwise OH^- is discharged as oxygen gas:

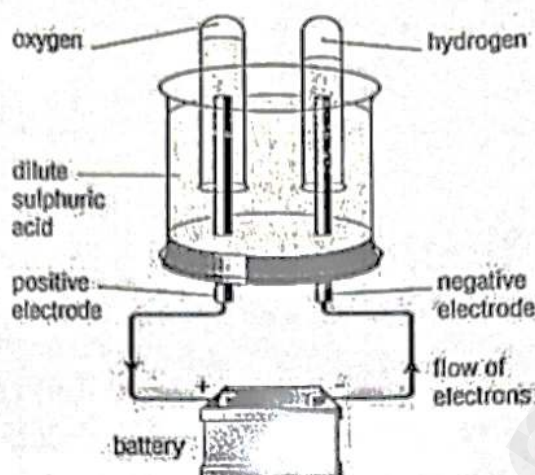


Na^+ and OH^- ions are left behind in solution, *leaving* forming aqueous sodium hydroxide. *not reaching*

* $\text{Cl}_{2(\text{g})}$ is only formed at the anode if the sodium chloride solution being used is concentrated. A dilute solution will give $\text{O}_{2(\text{g})}$ as the anode product. This rule also applies in the electrolysis of other halide aqueous solutions.

Apparatus for electrolysis of aqueous solutions e.g. $\text{H}_2\text{SO}_4(\text{aq})$

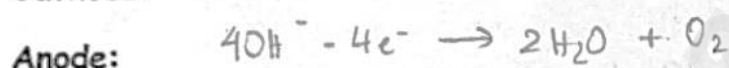
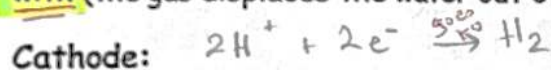
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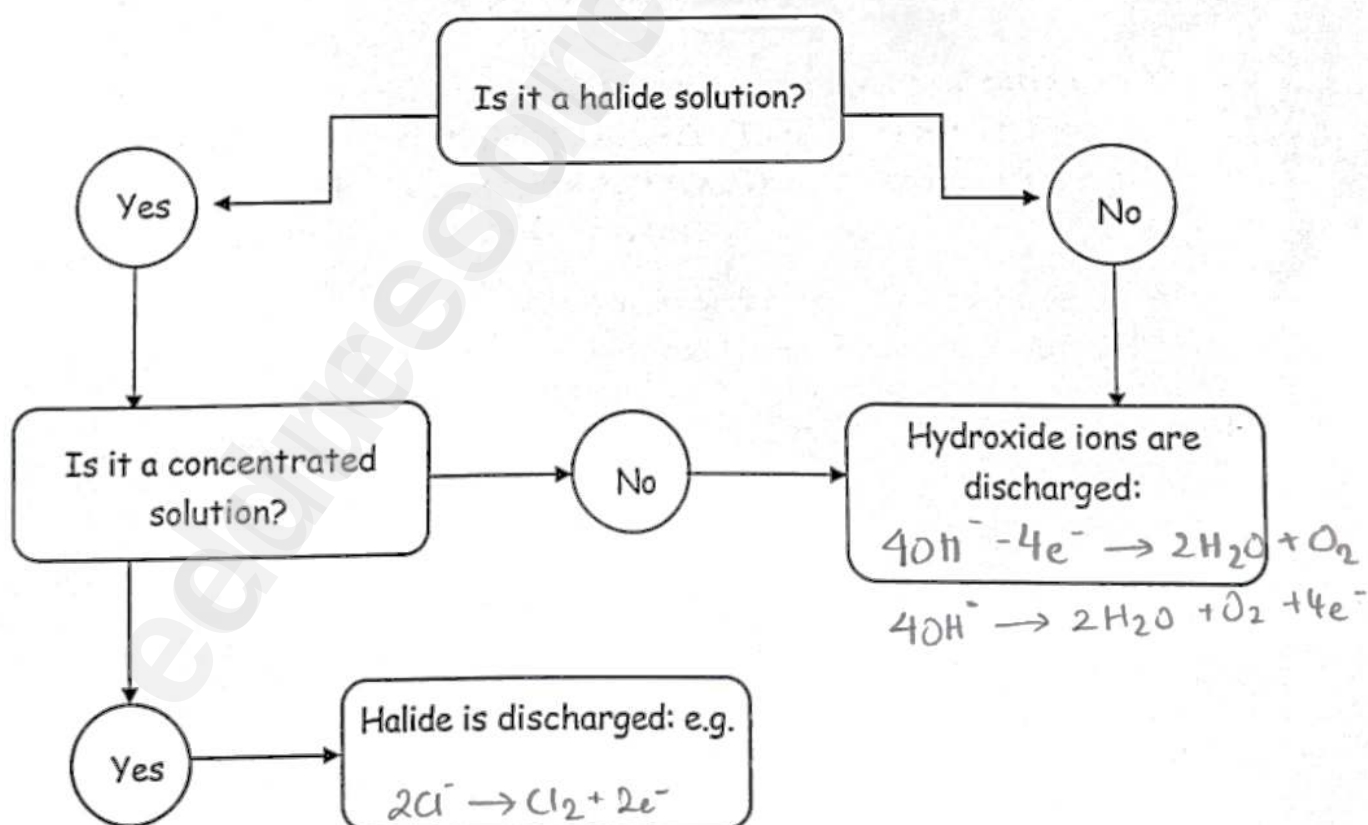
ANODE
→ Cathode

Because if the test tube was empty (it has air) so the gas will not flow to the tube.

In order for the gases to be collected, the test tubes must be filled with water to start with (the gas displaces the water out of the tube as it fills it).



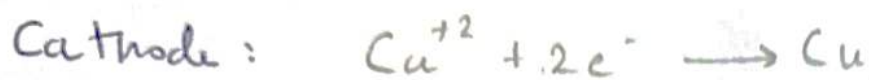
The Anode Rule for aqueous electrolysis



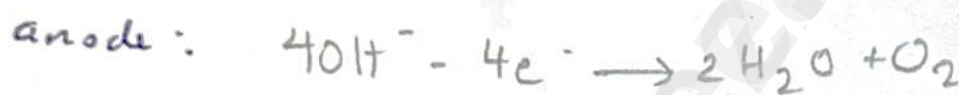
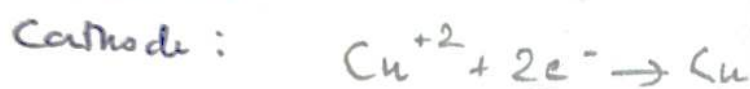
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Write the cathode and anode reactions for the following aq. solutions:

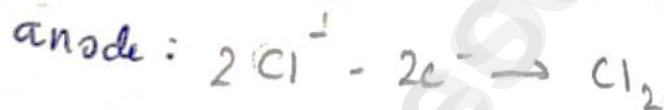
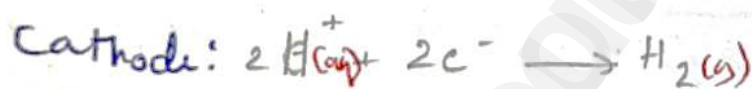
1. conc. $\text{Cu}(\text{NO}_3)_2$



2. Dilute CuCl_2



3. conc. CaCl_2



(write the ions present in the electrolyte.)

The rules for ion discharge during electrolysis

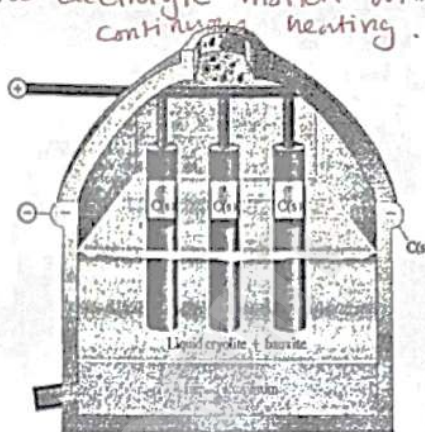
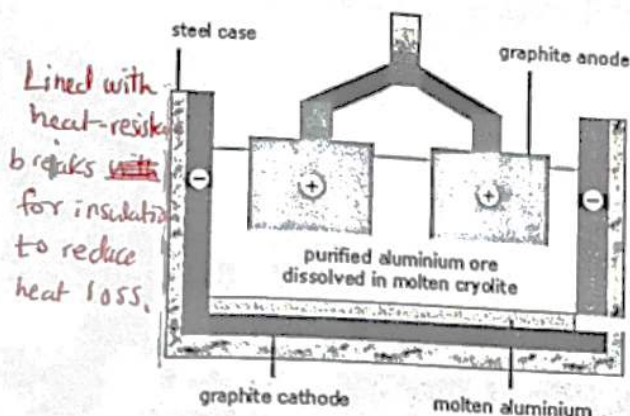
Electrolyte	Example	Electrodes	Cathode reaction	Anode reaction
Molten salt	PbBr ₂ (1)	Inert (1)	$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}(1)$	$2\text{Br}^- - 2\text{e}^- \rightarrow \text{Br}_{2(g)}$
Aqueous salt solution	NaCl _(aq) *	Inert	$2\text{H}^+_{(aq)} + 2\text{e}^- \rightarrow \text{H}_{2(g)}(2)$	$2\text{Cl}^- - 2\text{e}^- \rightarrow \text{Cl}_{2(g)}(3)$
	CuSO _{4(aq)}	Inert	$\text{Cu}^{2+}_{(aq)} + 2\text{e}^- \rightarrow \text{Cu}(s)$	$4\text{OH}^- - 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_{2(g)}$
Aqueous acid	HCl _(aq) *	Inert	$2\text{H}^+_{(aq)} + 2\text{e}^- \rightarrow \text{H}_{2(g)}$	$2\text{Cl}^- - 2\text{e}^- \rightarrow \text{Cl}_{2(g)}$
	H ₂ SO _{4(aq)}	Inert	$2\text{H}^+_{(aq)} + 2\text{e}^- \rightarrow \text{H}_{2(g)}$	$4\text{OH}^- - 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_{2(g)}$
Aqueous alkali	NaOH _(aq)	Inert	$2\text{H}^+_{(aq)} + 2\text{e}^- \rightarrow \text{H}_{2(g)}$	$4\text{OH}^- - 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_{2(g)}$
Aqueous salt solution	CuSO _{4(aq)}	Copper (active) (4)	$\text{Cu}^{2+}_{(aq)} + 2\text{e}^- \rightarrow \text{Cu}(s)$	$\text{Cu}(s) - 2\text{e}^- \rightarrow \text{Cu}^{2+}_{(aq)}(5)$

1. Inert Electrodes do not take part in the electrolysis reactions - they simply carry the current into and out of the electrolyte.
2. If the metal ion from the salt is below hydrogen in the metal reactivity series, then the metal is discharged at the cathode. (Exception is Zn, which is discharged although it's above H₂ in the reactivity series.) Otherwise, Hydrogen is discharged from the water.
3. If the non-metal ion from the salt is a halide (F⁻, Cl⁻, Br⁻, I⁻), then the Halogen is formed at the anode. Otherwise, Oxygen is formed from the hydroxide ions.
4. Active electrodes take part in the electrolysis reactions. (See electrolytic refining later.)
5. The anode, which is made of the same metal as the cation in the salt, dissolves as the electrolysis proceeds. The net result is the transfer of metal from the anode to the cathode. This is used in electroplating and electrolytic refining. (See later notes).

*These solutions must be concentrated in order for Cl_{2(g)} to be evolved at the anode, otherwise, O_{2(g)} may be evolved instead (from the discharge of OH⁻ ions).

Industrial manufacture of Aluminium (by Electrolysis)

The current of 100 kA generates enough energy to keep the electrolyte molten without the need for continuous heating.



NB: Pure aluminium oxide melts at 2000°C . Dissolving it in molten cryolite (Na_3AlF_6) cuts costs by lowering the melting point to around $950-1000^{\circ}\text{C}$.



The O_2 produced at the anode reacts with the carbon anode to form $\text{CO}_2(\text{g})$ which means that the anode needs to be replaced frequently.

at very high temperatures.
(not at low temp as carbon is unreactive)

- Expensive :
- ① electricity costs.
 - ② High melting point of bauxite.
 - ③ anode needs to be replaced frequently.

What keeps the electrolyte molten?

The current produced by the electricity produces heat energy which keeps the electrolyte molten so

How is aluminium collected?

- tapped off as a liquid.

Why is platinum not used instead of carbon as an anode?

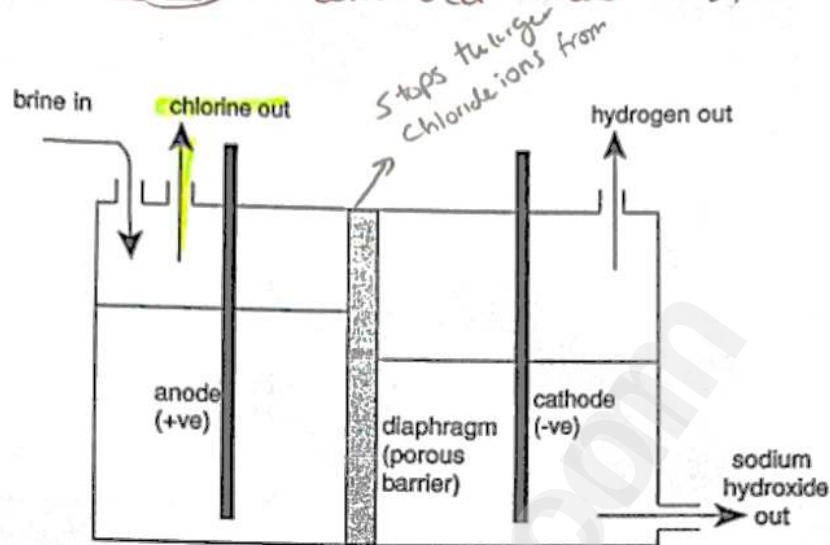
- It is very expensive. (although it conducts electricity)

Due to the high cost of this process, recycling is a good alternative.

The manufacture of Chlorine, Sodium Hydroxide and Hydrogen by the Electrolysis of Brine

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concentrated NaCl solution.



(The brine cell or membrane cell. Brine is concentrated aqueous sodium chloride.)

(The diaphragm stops chlorine from passing through.) while allowing the smaller particles to pass through eg H^+ , Na^+

Cathode	Anode
$2H^+ + 2e^- \rightarrow H_2$	$2Cl^- - 2e^- \rightarrow Cl_2$

Uses of chlorine

- > Bleach
- > Manufacture of plastics e.g. PVC

- > Sterilizing in drinking water
- > Killing bacteria in swimming pools.

Uses of hydrogen

- > Fuel
- > Manufacture of ammonia
- > Manufacture of margarine

sources of hydrogen

- ① reaction of natural gas with steam & heat
- ② electrolysis of brine

Test for chlorine = turns blue damp litmus paper red and bleaches it turning it white.

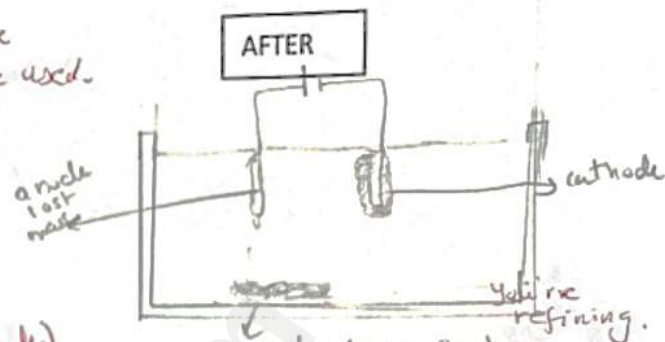
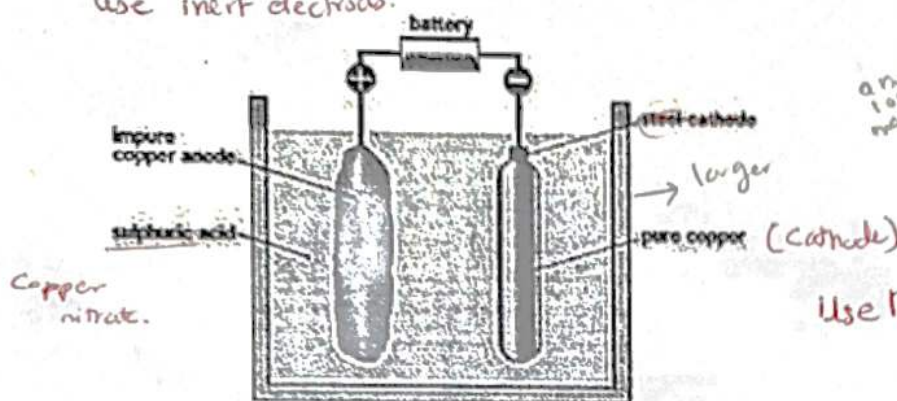
Using electrolysis for refining metals (Electrolytic Refining)

- Type of electrolysis

Purification

- Diff in that electrolytic cells use inert electrodes.

but here active electrodes are used.



Use the electrolyte of the metal
nitrate (as it is soluble)

The electrons go through the external circuit and will flow through the cathode

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

impurities fall off the impure copper anode (metal)

The solution, refers to the place where the copper atoms are going.

At the same time, copper atoms from the anode go into solution as $Cu^{2+}(aq)$ ions. (copper metal) (metal atoms)

describes the process atoms losing electrons and is going to electrolysis

$Cu^{+2}(aq)$ are attracted to the negative cathode and get discharged as copper atoms which makes the cathode larger while the anode becomes thinner. ✓

Thicker. ✓

Reasons why anode lost mass?

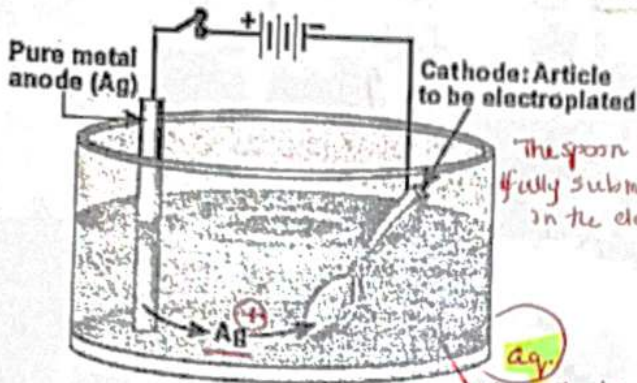
- ① Anode sludge fell off
- ② Copper atoms turn into ions in the solution.

How is electrolysis used in Electroplating?

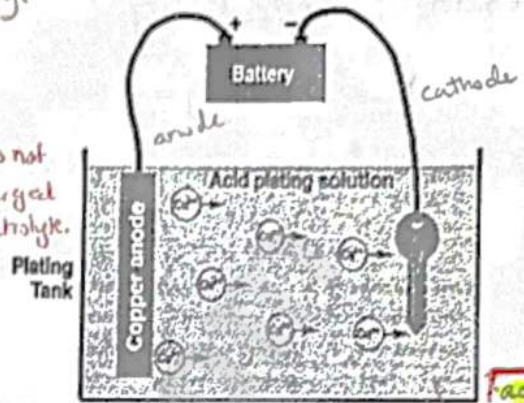
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electrolyte
metal
anode
cathode
electrolyte

- Why?
- ① preventing rusting
 - ② shiny.



Electroplating with silver



Typical plating experiment

First step in electroplating:

- ① prepare the object by cleaning it
- ② rotate the object regularly for even coating.

The spoon or the key is the cathode and it should be clean from dirt/grease (which would act as a barrier preventing the silver or copper from sticking properly to the object). The object could also be rotated to ensure an even coating.

Choose a metal nitrate solution.

Cations are attracted to the cathode where they gain electrons and are discharged as metal. At the anode (+ve) metal atoms become cations and go into solutions, replacing metal ions that are being discharged at the cathode.

	Cathode	Anode
KEY:	$\text{Cu}^{+2} + 2\text{e}^- \rightarrow \text{Cu}$	$\text{Cu} - 2\text{e}^- \rightarrow \text{Cu}^{+2}$
SPOON:	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	$\text{Ag} - \text{e}^- \rightarrow \text{Ag}^+$

To electroplate an object with a metal X

- > The object is used as the cathode
- > Metal X is used as the anode
- > A solution of a compound of X is used as the electrolyte. (preferably nitrates.)

Uses of electroplating

- > To protect objects from rusting/corrosion by electroplating with an unreactive metal.
- > To give an attractive, shiny finish, e.g. chromium plating on the car bumpers.

Why conc. of electrolyte doesn't change? (another reason why electrolyte is of the same metal).

- The electrolyte simply acts as a medium to transport the ions from anode to cathode.

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