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ELECTROLYTIC CELLS

1.) Electrolysis of CuCl_2 ✓

PbBr_2 ✓

H_2O ✓

2.) Electroplating ✓

3.) Purification of copper

4.) Aluminium industry ✓

* 5.) Chloro-alkali industry

- mercury cathode
- diaphragm
- membrane process

Differences between Galvanic and Electrolytic cells

Galvanic cell (voltaic cells)	Electrolytic cell (electroplating, electrolysis)
Uses a spontaneous redox reaction	Uses a non-spontaneous redox reaction
$E_{cell} > 0$ positive	$E_{cell} < 0$ negative
Converts chemical energy into electrical energy. i.e produces an electric current i.e NO power supply because it is a power supply	Converts electrical energy into chemical energy i.e uses an electric current i.e is connected to a power supply
Anode – negative electrode Cathode – positive electrode	Anode – positive electrode Cathode – negative electrode
Has a salt bridge	NO salt bridge present

↳ use to identify if image shows Galvanic or Electrolytic

Electrolytic Cells

These electrochemical cells convert electrical energy into chemical energy. Electrolytic cells use a non-spontaneous redox reaction. The energy for this non-spontaneous reaction is supplied by a power source. The power source could be cells, batteries or A.C power source. The process within an electrochemical cell is called Electrolysis.

Uses of electrolysis includes : electroplating metals with other metals

EPNS - electroplated nickel silver

Production of chlorine

Electrolysis of water

Hair removal

Production of Aluminium, Copper, etc

Reduction – the process that involves the gain of electrons

Oxidation – the process that involves the loss of electrons

In an electrolytic cell :

- the **anode** is the **positive electrode** (connected to the positive terminal of a battery)
- the **cathode** is the **negative electrode** (connected to the negative terminal of a battery)
- $E_{cell} = E_{red} - E_{oxi}$ will be a **NEGATIVE** number i.e $E_{cell} < 0$

If the cell potential / emf is $-1,8\text{ V}$ then this means that the electrolytic cell needs a minimum power supply / voltage of $1,8\text{ V}$ to work.

- When you use the redox table, the reaction at the cathode will be **above** the reaction at the anode.
- CROAK** - **cathode** reduction **anode** oxidation
- Metals have a positive charge (cations = positive ions) and will therefore be attracted to the negative electrode called the cathode. Non-metals have a negative charge (anions = negative ion) and will thus be attracted to the positive electrode called the anode.

Electroplating

Place the **metal at the Anode**

Place **object** (spoon, baby's shoe, magwheel) that is being plated at the **cathode**

Example Electroplating Copper onto a baby's shoe (bronzing)

Electrolyte: copper sulphate CuSO_4

Copper metal @ anode
Anode half reaction: $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$ (oxidation)

(shoe)
Cathode half reaction: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ (reduction)

↳ Cu transferred onto the shoe.

Why does the **colour** of the blue Copper sulphate electrolyte solution **remain blue**?

learn!

Answer: The **Copper sulphate** electrolyte solution has Cu^{2+} ions. As these ions "used up" during **reduction** at the cathode, **more Cu^{2+} ions** are produced at the **anode** during the oxidation of the Copper metal. Therefore, **keeping the concentration constant**.

During the **electroplating** of the shoe, the **current** was **1600 mA** and the time taken was **7,5 minutes**. The initial **mass** of the shoe was **800g**, calculate the **final mass**

$$\begin{aligned} \textcircled{1} \quad Q &= It \\ &= 1,6 \times 7,5 \times 60 \\ &= 720 \text{ C} \end{aligned} \quad 1600 \text{ mA} \div 1000 = 1,6 \text{ A}$$

$$\begin{aligned} \textcircled{2} \quad \text{Faraday's constant: } 96500 \text{ C of charge on 1 mol of e}^- \\ x = \frac{720}{96500} = 7,461 \times 10^{-3} \text{ mol of e}^- \end{aligned}$$

$$\begin{aligned} \textcircled{3} \quad \text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu} \\ \begin{array}{ccc} 1 & : & 2 \\ 7,461 \times 10^{-3} & & \end{array} = 3,731 \times 10^{-3} \text{ mol of Cu.} \end{aligned}$$

cathode: gains
 ↑
 ADD: mass gained

$$\begin{aligned} \textcircled{4} \quad m &= n \times M_r \\ &= 3,73 \times 10^{-3} \times 63,5 \\ &= 0,24 \text{ g DEPOSITED} \end{aligned}$$

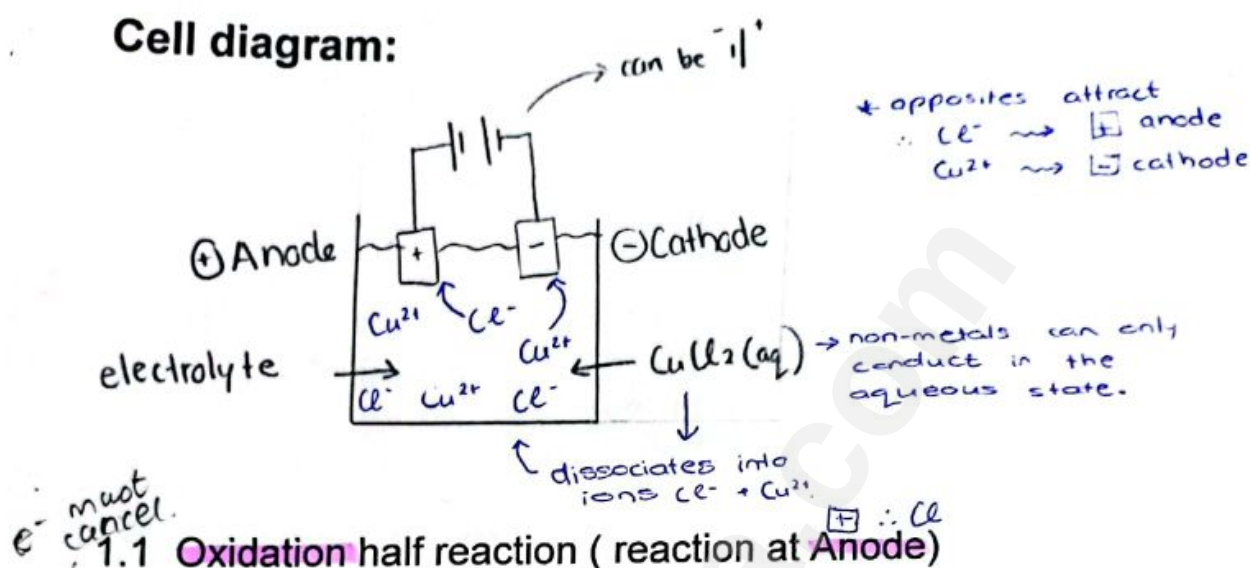
FINAL MASS:

$$\begin{aligned} 800 + 0,24 \\ = 800,24 \text{ g} \end{aligned}$$

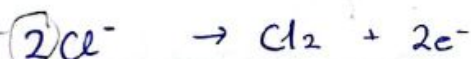
cathode
 anode

Example 1 : The electrolysis of Copper (II) chloride

Cell diagram:



1.1 **Oxidation** half reaction (reaction at **Anode**)



1.2 **Reduction** half reaction (reaction at **Cathode**)



1.3 **Net ionic** reaction :



1.4 **Energy conversion** : electrical energy to chemical energy

1.5 Which substance was **collected** at the **anode** ? Cl_2 gas
 What **observation** would you make ? bleach-like smell

1.6 Which **substance** was collected at the **cathode** ? Copper metal
 What **observation** would you make ? brown deposit

OVERALL BALANCED EQUATION:



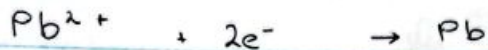
* opposites attract.

2.) Electrolysis of $PbBr_2$:

① Separate into ions

② Apply opposites attract

③ oxi / red ...

cathode : $\ominus$ (reduction)anode : $\oplus$ (oxidation)Net ionic :Volt : $E_{cell} = E_{red} - E_{oxi}$

$$= (-0.13) - (+1.09)$$

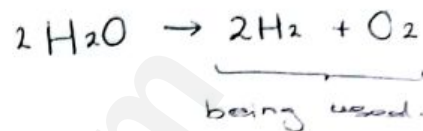
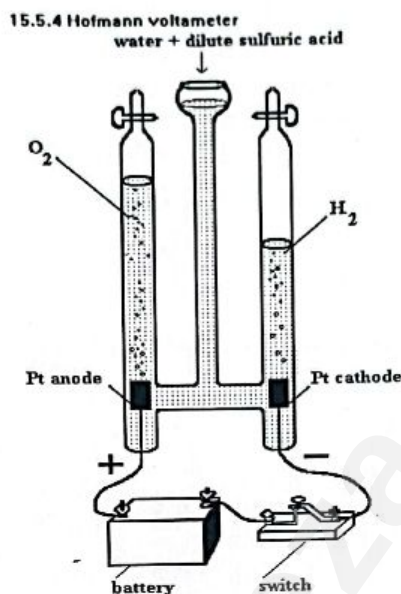
$$= -1.22 V$$

 $\ominus \therefore$ non-spontaneous $\therefore$ requires power supply with minimum $+1.22 V$.

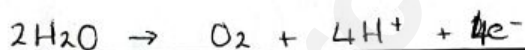
⊛

Example 3 : Electrolysis of Water

*NAME _____

In a school lab we use a **Hoffmann voltmeter**

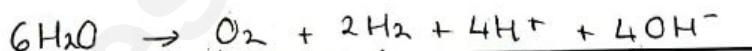
ALWAYS:

**2.1 Oxidation half reaction (reaction at Anode)**

→ Water making O

2.2 Reduction half reaction (reaction at Cathode)

→ water making H

2.3 Nett ionic reaction : → Remember to BALANCE e^- ! + same molecules**2.4 Balanced equation :** $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$ **2.5 Which substance was collected at the anode ?**

oxygen O

2.6 How would you test for the presence of this substance ?

Use a glowing splinter → it glows brighter in the presence of oxygen

2.7 Which substance was collected at the cathode ?

Hydrogen gas

↳ TEST: use a flame + listen for a popping sound.

* H_2O is the oxidising and reducing agent.

Aluminium Industry

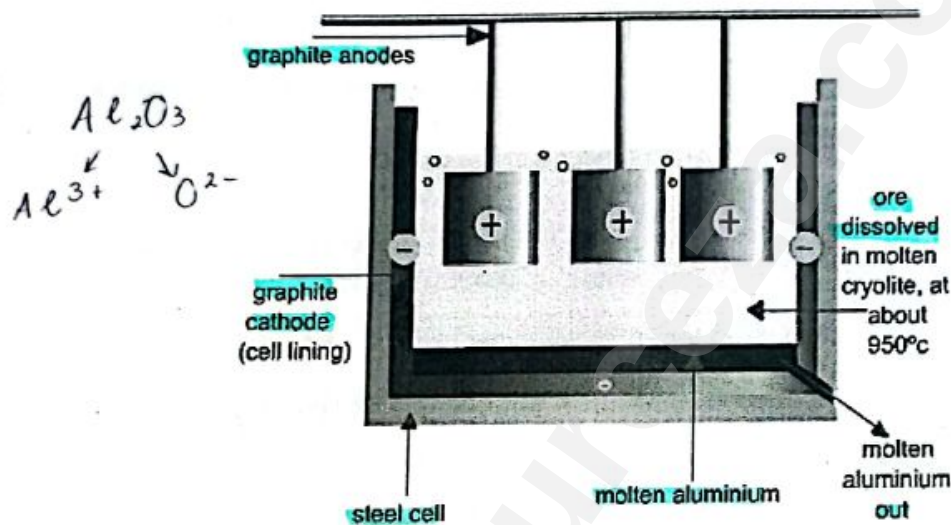
→ Hall process / Hall-Herbut

KNOW !

Aluminium is made by the electrolysis of its oxide called Bauxite: Aluminium oxide Al_2O_3 . The process is called the Hall Process. The oxide is obtained from the mineral bauxite – an impure and hydrated form (has water of crystallization) $Al_2O_3 \cdot xH_2O$

The melting point of bauxite is too high ($2050^\circ C$) and it can therefore not be used during electrolysis in its molten state. Expensive and energy consuming process. However, a mixture of bauxite and cryolite Na_3AlF_6 . It contains the complex ion AlF_6^{3-} which has a much lower melting point ($900^\circ C$). This mixture is electrolysed.

* in south Africa, it is



The anodes (positive electrodes) used are made from graphite. The cathode is the steel vessel / container. The container is also lined with graphite. The electrolyte is placed into the container.

The reaction at the cathode: red. $Al^{3+} + 3e^- \rightarrow Al(l)$

Learn * The reaction at the anode: ox. $2O^{2-} \rightarrow O_2(g) + 4e^-$
charge = -4 $\therefore 4e^-$

Problems associated with this industry:

1. The graphite electrodes are converted into carbon dioxide and must thus be replaced from time to time.
2. The energy consumption is high and the Hall process is only feasible if carried out near a cheap source of electricity. Example: near a wind or hydroelectric power plant

at anode:
 $C + O_2 \rightarrow CO_2$
pollution & greenhouse gas

↳ in SA: Richard's Bay (largest harbour).
3.) pollution

* What substance underwent reduction?

↳ Al^{3+}

Cathode: $4Al^{3+} \xrightarrow{12e^-} 4Al(s)$

ALUMINIUM INDUSTRY

ALUMINIUM

PROBLEMS

SOLUTIONS

- 1.) CO_2 produced at anode
 ↳ greenhouse gas
 ↳ pollutant

Use a fume hood to collect the released CO_2

- 2.) Cost of melting Al_2O_3 is very high

Add cryolite as it:

- lowers melting pt from 2050°C to 900°C
- acts as thermal insulator

- 3.) Cost of electricity is high
 + Coal-fired power stations produce CO_2 , SO_2 , NO_2
 ↳ pollutants + acid
 ↳ acid rain

Use Hydro-electric power from tidal waves.

- 4.) Anodes made from graphite get eroded
 ↳ $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$
 ∴ need to be replaced

x

NOTE: alleviation / solution to ALL → recycle aluminium

🐼 Purification of Copper

- Also called **Electro-refining** of Copper or **electro-winning**
- The **impure copper** is called **Blister Copper**

→ **Blister Copper**

The **impure mixture** of the **ORE** (mixture of **metals with minerals**) is placed at the **Anode**.

Copper, Platinum, Silver are in the impure mixture. **Copper** is a **stronger oxidising agent** ^{reducing} than the other 2 and will therefore **undergo oxidation 1st**. The **other impurities** will sink to the **bottom**.

Electrolyte: **aqueous Copper nitrate** or **Copper sulphate**.

Anode half reaction: $\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^-$ oxidation

Cathode half reaction: $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ reduction

The **Copper sulphate** or **Copper nitrate** electrolyte solution has **Cu^{2+} ions**. As these ions "**used up**" during **reduction** at the **cathode**, **more Cu^{2+} ions** are **produced** at the **anode** during the **oxidation** of the **Copper metal**. Therefore, keeping the **concentration constant**.
↳ positive ions move to negative cathode.

The **cathode** is made from **COPPER**. We collect **Copper** on a **copper electrode**.

↳ ∴ don't have to separate diff metals.

When all the **copper** has been **collected** and we now need to **collect the pure Silver**.

The following **changes** will be required:

- **Electrolyte Silver nitrate**
- **Cathode** must now be **Silver**
- **Adjust the Voltage** of the power supply

} know.

chloro-alkali industry

↳ chlorine gas product

↳ base NaOH product → Also called chloro-caustic

• NaOH used:

→ soaps
→ drain cleaner

• Cl₂

→ bleach
→ pool cleaner

• H₂

→ Haber-Bosch
→ Rocket fuel

1.) ORIGINAL PROCESS: Mercury cathode method/process

2.) Diaphragm process

3.) CURRENTLY USED: membrane process

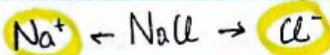
KNOW:

✓ method
✓ issues/reasons for disuse.

① MERCURY CATHODE PROCESS:

electrolyte: molten NaCl

↳ melts at $\pm 801^\circ\text{C}$ ($\therefore$ expensive to melt)



*opposite charges attract.

Anode: $\oplus$ $\therefore$ attracts Cl^-

oxidation: $2\text{Cl}^- \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$

↳ we collect $\text{Cl}_2(\text{g})$ at the anode

Cathode: $\ominus$ $\therefore$ attracts Na^+

reduction: $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}(\text{l})$ ← molten

↳ The liquid Sodium will be transported on a liquid mercury Hg layer. (recycled)

↳ We call this an amalgam

↳ $\frac{\text{Na}}{\text{Hg}}$ $\rightarrow$ less dense $\therefore$ floats
 $\rightarrow$ more dense $\therefore$ sinks

↳ $\text{Na} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{H}_2$

↳ We collect NaOH and $\text{H}_2(\text{g})$ at the CATHODE.

Net ionic: $2\text{Cl}^- \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$ } balance!
 $2\text{Na}^+ + 2\text{e}^- \rightarrow 2\text{Na}(\text{l})$



Cell: $E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}} = -2.71 - 1.36 = -4.07\text{V}$

minimum voltage required:

↳ 4.07V

! 4.07V - you

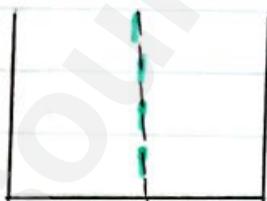
USES:

- NaOH → drain cleaner
→ soaps
- Cl_2 → bleach
→ pool cleaner
- H_2 → Haber-Bosch
→ Rocket fuel.

Problems with Mercury cathode process:

- ✓ Hg is a heavy metal that causes issues with the nervous system.
- ✓ cost of melting NaCl is high.
- ✓ cost of electricity is high.

2.) DIAPHRAGM PROCESS



diaphragm made from Asbestos:
→ separates anode from cathode

$\text{Na}^+ \neq \text{Na}$

electrolyte : aqueous NaCl → saltwater / "brine"

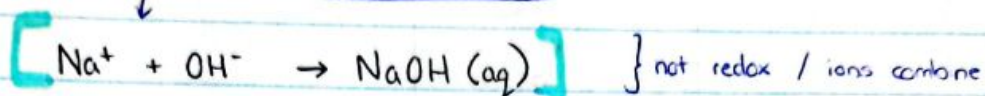
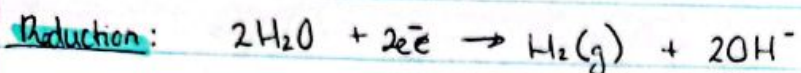
Cathode $\ominus$ (reduction) $\therefore$ attracts Na^+

- ↳ Na^+ will compete with water molecules (use redox table)
- ↳ water is a stronger oxidising agent than Na^+
- ↳ water will undergo reduction instead of Na^+ .

reduction of H_2O : $E = -0.83\text{V}$

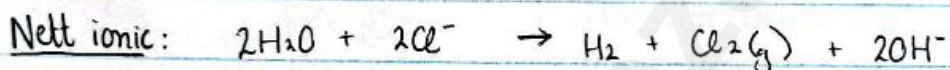
reduction of Na^+ : $E = -2.71\text{V}$

} $\therefore$ reduction of water is more energy efficient.



At cathode: - $\text{H}_2(\text{g})$ product
- NaOH collected.

Anode: $\oplus \therefore$ attracts Cl^-



$E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}} = -0.83 - 0.36 = -2.19 \text{ V}$

$\therefore$ min 2.19V supply needed.

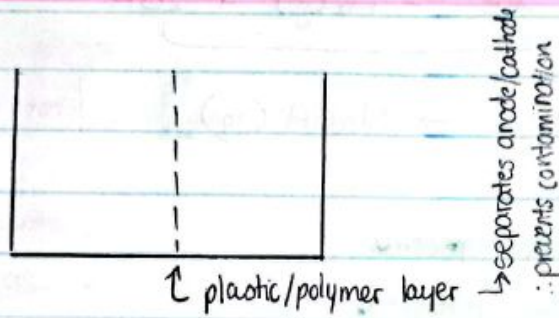
* minimum voltage required is less than in the mercury cell

Problems: with diaphragm process:

- ✓ Asbestos is carcinogenic (causes cancer)
- ✓ causes respiratory problems
- ✓ ✓

* products made in the mercury cell or diaphragm cell are contaminated with mercury or asbestos $\therefore$ low quality + purity.

Membrane Cell



- ✓ less contamination
- ✓ fewer health-related issues
- ✓ products are of high quality/purity

+ plastic membrane is selectively permeable ∴ only allows certain ions (Na^+) through.

* Learn all reactions as per diaphragm (incl. Ecell).

MERCURY CATHODE PROCESS	DIAPHRAGM PROCESS	MEMBRANE PROCESS
Electrolyte: molten NaCl → salt Anode: (oxidation) $2\text{Cl}^- \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$ ⊕ attracts Cl^- ∴ $\text{Cl}_2(\text{g})$ collected Cathode: (reduction) ⊖ attracts Na^+ $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}(\text{l})$ ∴ NaOH and H_2 collected. $\text{Na} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{H}_2$ ∴ Na(l) transported on denser Hg layer called an amalgam. Net ionic: * Balance e⁻ of half reactions! $2\text{Na}^+ + 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{Na}$ E_{cell}: $E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$ $= -2.71 - 1.36 = -4.07\text{V}$ ∴ minimum voltage of 4.07V required as power supply. Problems: • Hg is a heavy metal that causes issues with the nervous system. • cost of melting NaCl is high (m.p.: 801°C). • cost of electricity is high. • contaminated with Hg ∴ low quality/purity.	Electrolyte: NaCl (aq) → saltwater / brine Anode: (oxidation) $2\text{Cl}^- \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$ ⊕ attracts Cl^- ∴ $\text{Cl}_2(\text{g})$ collected Cathode: (reduction) ⊖ attracts Na^+ $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-$ ∴ $\text{H}_2(\text{g})$ & NaOH collected. $\text{Na}^+ + \text{OH}^- \rightarrow \text{NaOH}(\text{aq})$ • Not competing with H_2O ∴ H_2O is a stronger oxid agent ∴ H_2O undergoes reduction → more energy efficient. Net ionic: $2\text{H}_2\text{O} + 2\text{Cl}^- \rightarrow \text{H}_2 + \text{Cl}_2(\text{g}) + 2\text{OH}^-$ E_{cell}: $E_{\text{cell}} = E_{\text{red}} - E_{\text{ox}}$ $= -0.83 - 0.36 = -2.19\text{V}$ ∴ minimum voltage of 2.19V needed. Problems: • Asbestos (used as membrane) is carcinogenic ∴ causes cancer. • respiratory problems • contaminated with asbestos ∴ low quality/purity.	IMPROVEMENTS: ✓ plastic/polymer membrane ↳ separates anode & cathode ↳ selectively permeable ↳ cationic membrane ∴ only Na^+ ✓ less contamination ✓ fewer health-related issues ✓ high quality/purity products