Cambridge (CIE) A Level Chemistry

Your notes

Electrolysis

Contents

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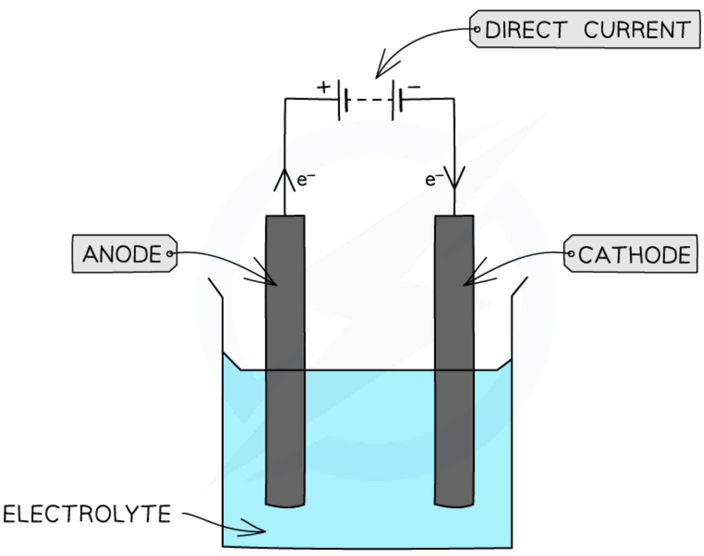
Products of Electrolysis

- **Electrolysis** is the breaking down of a compound into its elements using an **electric current**
- For example, the electrolysis of zinc chloride ($ZnCl_2$) into its elements zinc and chlorine

$$ZnCl_2 \rightarrow Zn + Cl_2$$

- This method is often used to:
    - Extract **metals** from their **metal ores** when the metals cannot be extracted by heating their ores with carbon
    - Purify metals
    - Produce non-metals such as fluorine
- Electrolysis is carried out in an electrolysis cell which consists of:
    - An **electrolyte** - this is the compound that is broken down during electrolysis and it is either a **molten ionic compound** or a **concentrated aqueous solution of ions**
    - Two **electrodes** - these are metal or graphite rods conduct electricity to the electrolyte and away from the electrolyte
        - The positive electrode is called the **anode**
        - The negative electrode is called the **cathode**
    - The power supply, which is **direct current**

An electrochemical cell



Electrolysis takes place in an electrochemical cell; this type of electrochemical cell is called an electrolytic cell

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Electrolysis of molten electrolytes

- **Cations** (positively charged ions) move to the **negatively charged cathode** where they **gain electrons**
  - **Reduction** takes place at the cathode
  - If a **metal** is formed, a layer of metal is deposited on a cathode or it forms a **molten layer** in the cell
  - If **hydrogen** gas is formed, bubbles are seen
  - For example, silver and hydrogen both form positively charged ions which would be **reduced** at the cathode as follows:

$$Ag^+ + e^- \rightarrow Ag$$

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

- **Anions** (negatively charged ions) move to the **positively charged anode** where they **lose electrons**
  - **Oxidation** takes place at the anode
  - For example, bromine forms negatively charged ions which would be **oxidised** at the anode as follows:

$$2Br^- \rightarrow Br_2 + 2e^-$$

Products formed by electrolysis when a pure molten ionic compound containing two simple ions is electrolysed

- Al_2O_3
  - Cathode = Al
  - Anode = O_2
- $MgBr_2$
  - Cathode = Mg
  - Anode = Br_2
- NaCl
  - Cathode = Na
  - Anode = Cl_2
- ZnI_2
  - Cathode =Zn
  - Anode = I_2

Electrolysis of aqueous solutions

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- **Aqueous solutions** have more than one cation and anion in solution due to the presence of **water**
- Water contributes H^+ and OH^- ions to the solution, which makes things more complicated
  - Water is a weak electrolyte and splits into H^+ and OH^- ions as follows:

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

- The actual ions that are **discharged** during electrolysis will depend on:
  - The relative electrode potential of the ions
  - The concentration of the ions

Relative electrode potential of ions

- The **relative electrode potential** (E^θ) of ions describes how easily an ion is discharged during electrolysis
- The **positively charged cation** with the most **positive** E^θ will be discharged at the **cathode** as this is the cation that is most easily **reduced**
  - For example, a concentrated **aqueous solution** of NaF will contain hydrogen (H^+) and sodium (Na^+) ions
  - The half-equations for the reduction of these ions and their E^θ values are as follows:

$$2H^+ (aq) + 2e^- \rightleftharpoons H_2 (g) \quad E^\theta = 0.00 \text{ V}$$

$$Na^+ (aq) + e^- \rightleftharpoons Na (s) \quad E^\theta = -2.71 \text{ V}$$

- Since H^+ ions have a higher E^θ value, hydrogen gas (H_2) is formed at the **cathode** instead of sodium (Na)
- The negatively charged anion that is **most easily oxidised** will be discharged at the **anode**
- This corresponds to the half-reaction with the **least positive** (or most negative) E^θ
  - For example, a concentrated aqueous solution of NaF will contain hydroxide (OH^-) and fluoride (F^-) ions
  - The half-equations for the reduction of the products and their E^θ values are as follows (this is the standard way they are shown in data booklets):

$$O_2 (g) + 2H_2O (l) + 4e^- \rightleftharpoons 4OH^- (aq) \quad E^\theta = +0.40 \text{ V}$$

$$F_2 (g) + 2e^- \rightleftharpoons 2F^- (aq) \quad E^\theta = +2.87 \text{ V}$$

- Since the OH^-/O_2 half-reaction has a **less positive E^θ value** (+0.40 V) than the F^-/F_2 half-reaction (+2.87 V), hydroxide ions are **more easily oxidised** than fluoride ions
  - Therefore, **oxygen (O_2) gas is formed at the anode**

Concentration of ions

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- Ions that are present in **higher concentrations** are more likely to be discharged
- For example, when a **concentrated** solution of NaF is electrolysed, there are far more **fluoride** ions which are discharged at the anode, instead of the **hydroxide** ions as the fluoride ions are in higher concentration
  - So, mainly fluorine will form at the electrode
- However, if a **very dilute** solution of NaF is electrolysed, there will be much more **oxygen** and much less fluorine gas formed at the anode
  - In reality, a mixture of both oxygen and fluorine gas is formed

Examiner Tips and Tricks

Electrolysis is a redox reaction as a reduction reaction takes place at one electrode and an oxidation reaction at the other electrode

When writing the overall redox equation make sure that the electrons lost at the anode balance the electrons gained at the cathode

For example:

- Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$
- Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$
- Overall: $CuCl_2 \rightarrow Cu + Cl_2$

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Faraday's Law

- The **amount** of substance that is formed at an electrode during **electrolysis** is proportional to:
    - The amount of **time** where a constant current to passes
    - The **amount of charge**, in coulombs, that passes through the electrolyte (strength of electric **current**)
    - The relationship between the current and time is:

$$Q = I \times t$$

- **Q** = charge (coulombs, C)
    - **I** = current (amperes, A)
    - **t** = time, (seconds, s)
- The **amount** or the **quantity of electricity** can also be expressed by the **faraday (*F*)** unit
    - One faraday is the amount of **electric charge** carried by 1 mole of electrons or 1 mole of singly charged ions
    - 1 faraday is 96 500 C mol^{-1}
    - Thus, the relationship between the Faraday constant and the Avogadro constant (*L*) is:

$$F = L \times e$$

- **F** = Faraday's constant (96 500 C mol^{-1})
    - **L** = Avogadro's constant (6.02×10^{23} mol^{-1})
    - **e** = charge on an electron

Worked Example

Determine the amount of electricity required for the following reactions:

1) To deposit 1 mol of sodium

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

2) To deposit 1 mol of magnesium

$$Mg^{2+} (aq) + 2e^- \rightarrow Mg (s)$$

3) To form 1 mol of fluorine gas

$$2F^-(aq) \rightarrow F_2(g) + 2e^-$$

4) To form 1 mole of oxygen

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

Answers:

- One Faraday is the amount of charge (96 500 C) carried by 1 mole of electrons

Answer 1:

- As there is one mole of electrons, one faraday of electricity (96 500 C) is needed to deposit one mole of sodium.

Answer 2:

- Now, there are two moles of electrons, therefore, two faradays of electricity (2 x 96 500 C) are required to deposit one mole of magnesium.

Answer 3:

- Two moles of electrons are released, so it requires two faradays of electricity (2 x 96 500 C) to form one mole of fluorine gas.

Answer 4:

- Four moles of electrons are released, therefore it requires four faradays of electricity (4 x 96 500 C) to form one mole of oxygen gas.

Determining Avogadro's Constant by Electrolysis

- The Avogadro's constant (L) is the number of entities in **one mole**
  - $L = 6.02 \times 10^{23}\ mol^{-1}$
  - For example, **four moles** of water contains 2.41×10^{24} ($6.02 \times 10^{23} \times 4$) molecules of H_2O
- The value of L ($6.02 \times 10^{23}\ mol^{-1}$) can be **experimentally** determined by electrolysis using the following equation:

$$L = \frac{\text{charge on 1 mol of electrons}}{\text{charge on 1 electron}}$$

Finding L experimentally

- The charge on **one mole of electrons** is found by using a simple **electrolysis** experiment using copper electrodes

Apparatus set-up for finding the value of L experimentally

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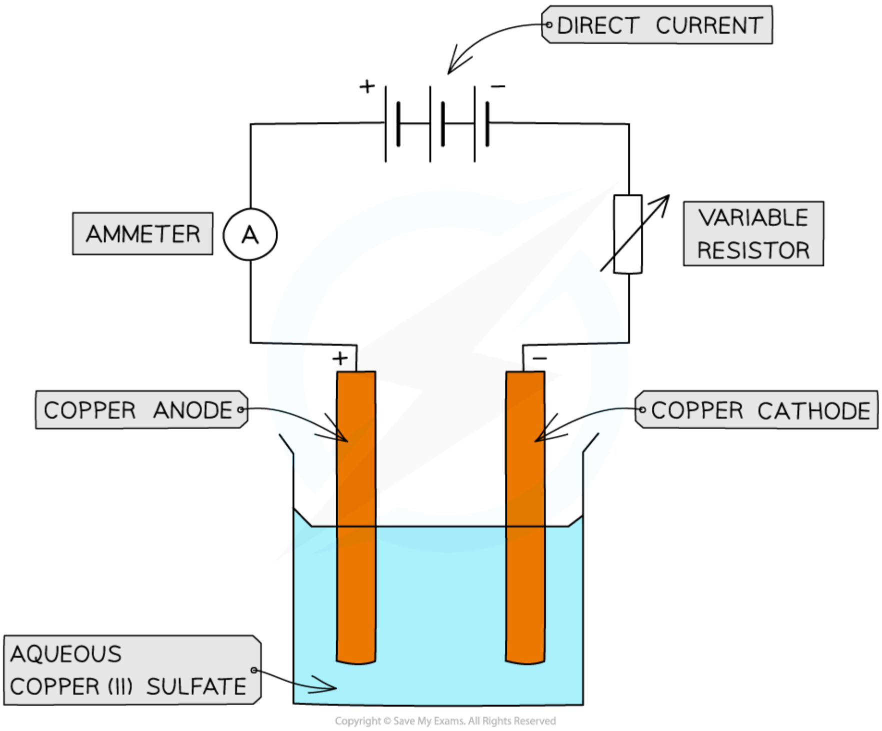

Electrolysis of copper(II) sulfate solution

- **Method**
  - The pure copper **anode** and pure copper **cathode** are **weighed**
  - A **variable resistor** is kept at a constant current of about 0.17 A
  - An **electric current** is then passed through for a certain time interval (e.g. 40 minutes)
  - The anode and cathode are then removed, washed with distilled water, dried with propanone, and then **reweighed**
- **Results**
  - The **cathode** has **increased** in mass as copper is deposited
  - The **anode** has **decreased** in mass as the copper goes into solution as copper ions
  - Often, it is the decreased mass of the anode which is used in the calculation, as the solid copper formed at the cathode does not always stick to the cathode properly
  - Let's say the amount of copper deposited in this experiment was 0.13 g
- **Calculation:**
  - The amount of charge passed can be calculated as follows:

$$Q = I \times t$$

$$= 0.17 \times (60 \times 40)$$

$$= 408 \text{ C}$$

- To deposit 0.13 g of copper (2.0×10^{-3} mol), 408 C of electricity was needed
- The amount of electricity needed to deposit 1 mole of copper can therefore be calculated using simple proportion using the relative atomic mass of Cu

Calculating the amount of charge required to deposit one mole of copper table

- To scale our experimental results up to the molar level, we can use a ratio method
- The scaling factor tells us how many times larger our target amount (1 mole) is compared to our experimental result.

Charge (C)	Scaling factor	Amount of Cu deposited (g)
408	$\frac{63.5}{0.13}$ = 488.5	0.13
$\frac{63.5}{0.13} \times 408 = 199{,}292$	1 (the target is 488.5 times bigger	63.5

- Therefore, 199 292 C of electricity is needed to deposit 1 mole of Cu
- The half-equation shows that **2 mol of electrons** are needed to deposit one mol of copper:

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

- So, the charge on **1 mol** of electrons is:
  - $Q = \frac{199\ 292}{2} = 99\ 646\ C$
- Given that the charge on **one electron** is 1.60×10^{-19} C, then L equals:
  - $L = \frac{\text{charge on 1 mol of electrons}}{\text{charge on 1 electron}}$
  - $L = \frac{99\ 646}{1.60 \times 10^{-19}} = 6.23 \times 10^{23}\ mol^{-1}$
- The **experimentally determined** value for L of $6.23 \times 10^{23}\ mol^{-1}$ is very close to the **theoretical** value of $6.02 \times 10^{23}\ mol^{-1}$

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Electrolysis Calculations

- **Faraday's constant** can be used to calculate:
  - The **mass** of a substance **deposited** at an electrode
  - The **volume** of gas **liberated** at an electrode

Calculating the mass of a substance deposited at an electrode

- To calculate the mass of a substance deposited at the electrode, you need to be able to:
  - Write the half-equation at the electrode
  - Determine the number of coulombs needed to form one mole of substance at the specific electrode using Faraday's constant
  - Calculate the charge transferred during electrolysis
  - Use simple proportion and the relative atomic mass of the substance to find its mass

Worked Example

Calculate the amount of magnesium deposited when a current of 2.20 A flows through the molten bromide for 15 minutes.

Answer:

- The magnesium (Mg^{2+}) ion is a positively charged cation that will move towards the cathode.
- **Step 1:** Write the half-equation at the cathode

$$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$$

1 mol **2 mol** **1 mol**

- **Step 2:** Determine the number of coulombs required to deposit one mole of magnesium at the cathode

For every one mole of electrons, the number of coulombs needed is 96 500 C mol^{-1}

In this case, there are **two moles** of electrons required

So, the number of coulombs needed is:

$$F = 2 \times 96\,500$$

$$F = 193\,000 \text{ C mol}^{-1}$$

- **Step 3:** Calculate the charge transferred during the electrolysis

$$Q = I \times t$$

$$Q = 2.20 \times (60 \times 15) = 1980 \text{ C}$$

- **Step 4:** Calculate the mass of magnesium deposited by simple proportion using the relative atomic mass of Mg

Charge (C)	Amount of Mg deposited (mol)	Amount of Mg deposited (g)
193 000	1	24.3
1980	$\frac{1980}{193\ 000} = 0.0103$	$0.0103 \times 24.3 = 0.25$

- Therefore, 0.25 g of magnesium is deposited at the cathode

Calculating the volume of gas liberated at an electrode

- To calculate the volume of gas liberated at an electrode, you need to be able to:
  - Write the half-equation at the electrode
  - Determine the number of coulombs needed to form one mole of substance at the specific electrode using Faraday's constant
  - Calculate the charge transferred during electrolysis
  - Use simple proportion and the relationship 1 mol of gas occupies 24.0 dm^3 at room temperature

Worked Example

Calculate the volume of **oxygen** gas produced at room temperature, when a concentrated aqueous solution of sulfuric acid, H_2SO_4, is electrolysed for 35.0 minutes using a current of 0.75 A.

Answer:

- The oxygen gas is formed from the **oxidation** of negatively charged hydroxide (OH^-) ions at the anode-
- **Step 1:** Write the half-equation at the anode

$$\mathbf{4}OH^-(aq) \rightarrow O_2(g) + \mathbf{2}H_2O(l) + 4e^-$$

4 mol 1 mol 2 mol 4 mol

- **Step 2:** Determine the number of coulombs required to form one mole of oxygen gas at the anode

For every one mole of electrons, the number of coulombs needed is 96 500 C mol^{-1}

So, for **four moles** of electrons, the number of coulombs needed is:

$$F = 4 \times 96\,500$$

$$F = 386\,000 \text{ C mol}^{-1}$$

Your notes

- **Step 3:** Calculate the charge transferred during the electrolysis

$$Q = I \times t$$

$$Q = 0.75 \times (60 \times 35) = 1575 \text{ C}$$

- **Step 4:** Calculate the volume of oxygen liberated by simple proportion using the relationship 1 mol of gas occupies 24.0 dm^3 at room temperature

Charge (C)	Amount of O_2 liberated (mol)	Amount of O_2 liberated (dm^3)
386 000	1	24
1575	$\frac{1575}{386\ 000} = 4.080 \times 10^{-3}$	$4.080 \times 10^{-3} \times 24.0 = 0.0979$

- Therefore, 0.0979 dm^3 of oxygen is formed at the anode

Worked Example

Calculating the volume of **hydrogen** gas produced at room temperature, when a concentrated aqueous solution of sodium sulfate, Na_2SO_4, is electrolysed for 17.5 minutes using a current of 3.25 A.

The hydrogen gas is formed from the **reduction** of positively charged hydrogen ions, H^+ at the cathode.

Answer:

- **Step 1:** Write the half-equation at the cathode

$$\mathbf{2H^+ (aq) + 2e^- \rightarrow H_2 (g)}$$

2 mols   2 mols   1 mol

- **Step 2:** Determine the number of coulombs required to form one mole of hydrogen gas at the cathode
  - For every one mole of electrons, the number of coulombs needed is:

$$F = 96\,500 \text{ C mol}^{-1}$$

$$F = 1 \times 96\,500$$

$$F = 96\,500 \text{ C}$$

- So, for **two moles** of electrons, the number of coulombs needed is:

$$F = 2 \times 96\,500$$

$$F = 193\,000 \text{ C}$$

- **Step 3:** Calculate the charge transferred during the electrolysis

$$Q = I \times t$$

$$Q = 3.25 \times (60 \times 17.5) = 3\,413 \text{ C}$$

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- **Step 4:** Calculate the volume of hydrogen liberated by simple proportion using the relationship 1 mol of gas occupies 24.0 dm^3 at room temperature

Charge (C)	Amount of H_2 liberated (mol)	Amount of H_2 liberated (dm^3)
193 000	1	24
3413	$\frac{3413}{193\ 000} = 1.76 \times 10^{-2}$	$1.76 \times 10^{-2} \times 24 = 0.42$

- Therefore, 0.42 dm^3 of hydrogen is formed at the cathode

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