

Electrolysis

Electrolytic cells convert electrical energy to chemical energy, by bringing about non-spontaneous processes.

$F = Le$ connects the Faraday constant, the Avogadro constant and the charge on the electron

F = Faraday constant (a measure of the charge of 1 mole of electrons = 96320 coulombs

L = Avogadro constant = 6.022×10^{23} e = charge of on electron = 1.60×10^{-19} coulombs.

Electrolysis of molten salts

When a simple ionic compound is electrolysed in the molten state using inert electrodes, the salt splits and the metal ion moves to the negative electrode and the negative ion moves to the positive electrode
e.g. if molten lead bromide is electrolysed, the lead will form at the negative electrode and bromine will form at the positive electrode

At the negative electrode (cathode)

At the negative electrode, positively charged ions **gain electrons** to become metal atoms.

This is classed as reduction. **Reduction** is gaining electrons

$\text{Na}^+ (\text{l}) + \text{e}^- \rightarrow \text{Na} (\text{s})$ (sodium ions become sodium atoms)

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

$\text{Al}^{3+} (\text{l}) + 3\text{e}^- \rightarrow \text{Al} (\text{s})$

At the positive electrode (anode)

At the positive electrode, negatively charged ions **lose electrons**.

This is classed as **oxidation**. Oxidation is losing electrons

$2\text{Cl}^- (\text{l}) \rightarrow \text{Cl}_2 (\text{g}) + 2\text{e}^-$ (chloride ions becomes chlorine)

$2\text{Br}^- (\text{l}) \rightarrow \text{Br}_2 (\text{l}) + 2\text{e}^-$ (bromide ions becomes bromine)

$2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$ (Iodide ions becomes Iodine)

$2\text{O}^{2-} (\text{l}) \rightarrow \text{O}_2 (\text{g}) + 4\text{e}^-$ (oxide ions becomes oxygen)

OIL RIG can help remember that **O**xidation is **L**oss of electrons:
Reduction is **G**ain of electrons

Electrolysing aqueous solutions

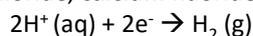
If an aqueous solution is electrolysed, using inert electrodes, the ions discharged depend on the electrode potentials of the ions involved.

In aqueous solutions there is a mixture of ions: H^+ and OH^- ions are present in addition to the ions from the salt
e.g. in copper chloride solution there are H^+ , OH^- (from water) Cu^{2+} , Cl^- (from the salt)

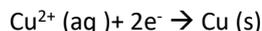
The negative electrode

At the negative electrode (cathode) in aqueous mixtures the cation with the **more positive electrode potential discharges**.

In **aqueous** solutions where the metal is more negative in the electrochemical series than hydrogen, the metal will not be evolved at the cathode. (e.g. **sodium** chloride, **calcium** fluoride) **Hydrogen gas** will be evolved at the cathode instead.



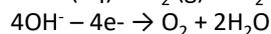
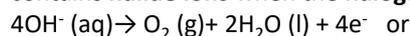
In **aqueous** solutions where the metal has a more positive E° value than hydrogen in the electrochemical series (e.g. **copper** chloride or **silver** fluoride,) the **metal** will be evolved at the cathode.



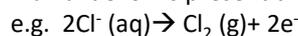
This happens because in the aqueous solution water molecules break down producing hydrogen ions and hydroxide ions that are discharged.

The positive electrode

At the positive electrode (anode), **oxygen** is produced unless the solution contains **halide ions** when the **halogen** is produced.



If a halide ion is present then the halogen is produced



The concentration of the negative ion can change the product evolved. A concentrated solution of sodium chloride, would give mostly chlorine gas. With increasingly dilute solutions, less chlorine and more oxygen will be evolved

Calculations with Electrolysis

Various questions can be asked using the following equations and constants (found in data book)

charge passed (in Coulombs) = current x time (in secs)

$$F = 9.65 \times 10^4 \text{ C mol}^{-1}$$

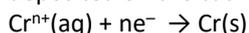
Moles of electrons = charge (in C) / F

$$\text{electronic charge } e = -1.60 \times 10^{-19} \text{ C}$$

Number of electrons passed = charge (in C) / electronic charge e

Example

A chromium salt was electrolysed. The chromium metal is deposited on the cathode, according to the following equation.



A current of 1.2 A was passed for 50 minutes through a solution of the chromium salt. 0.647 g of chromium was deposited.

Calculate the value of n in the above equation.

charge passed (in Coulombs) = current x time (in secs)

$$\text{charge passed} = 1.2 \times 50 \times 60 = 3600 \text{ C}$$

Moles of electrons = charge (in C) / F

$$\text{Mole of } \text{e}^- = 3600 / 96500 = 3.731 \times 10^{-2} \text{ mol}$$

$$\begin{aligned} \text{Moles of Cr} &= \text{mass} / M_r = 0.647 / 52 \\ &= 1.244 \times 10^{-2} \text{ mol} \end{aligned}$$

n = moles of electrons / moles of Cr

$$n = 3.731 \times 10^{-2} / 1.244 \times 10^{-2}$$

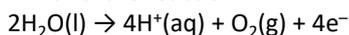
$$= 3.00$$

Example: Calculating Avogadro's constant

A current of 1.8 A was passed through dilute sulfuric acid for 30 minutes. 195 cm³ of oxygen was collected at the anode.

Conditions were 25 °C and 1 atm.

This is the reaction:



Calculate a value for the Avogadro constant, L

moles of O₂ made = gas volume of O₂ / molar volume

$$\begin{aligned} \text{moles of O}_2 &= 0.195 \text{ (dm}^3\text{)} / 24 \\ &= 8.125 \times 10^{-3} \text{ mol} \end{aligned}$$

Using balanced equation

$$\begin{aligned} \text{moles of electrons made} &= 4 \times 8.125 \times 10^{-3} \\ &= 3.25 \times 10^{-2} \text{ mol} \end{aligned}$$

charge passed (in Coulombs) = current x time (in secs)

$$\text{charge passed} = 1.8 \times 30 \times 60 = 3240 \text{ C}$$

Number of electrons passed = charge (in C) / electronic charge e

$$\begin{aligned} &= 3240 / 1.6 \times 10^{-19} \\ &= 2.025 \times 10^{22} \end{aligned}$$

Avogadro constant, L = number of electrons passed / moles of electrons

$$= 2.025 \times 10^{22} / 3.25 \times 10^{-2} = 6.2 \times 10^{23} \text{ mol}^{-1}$$