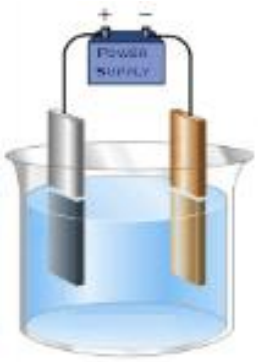
Electrolytic Cell (Part 2)



Content

- Electrolysis
  (i) factors affecting the amount of substance liberated during electrolysis
  (ii) the Faraday constant; the Avogadro constant; their relationship
  (iii) industrial uses of electrolysis

Learning Outcomes

Candidates should be able to:

(l) state the relationship, F = Le, between the Faraday constant, the Avogadro constant and the charge on the electron

(m) predict the identity of the substance liberated during electrolysis from the state of electrolyte (molten or aqueous), position in the redox series (electrode potential) and concentration

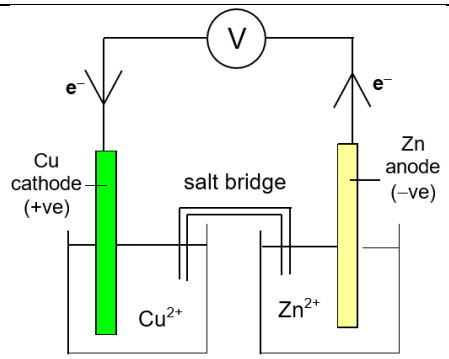
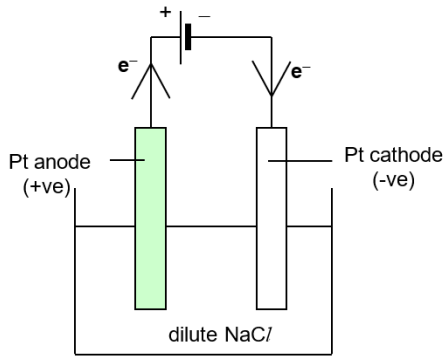
(n) calculate:
  (i) the quantity of charge passed during electrolysis
  (ii) the mass and/or volume of substance liberated during electrolysis

(o) explain, in terms of the electrode reactions, the industrial processes of:
  (i) the anodising of aluminium
  (ii) the electrolytic purification of copper [technical details are not required]

References

- Advanced Chemistry, by Michael Clugston and Rosalind Flemming.
- Chemistry for Advanced Level, by Peter Cann and Peter Hughes
- Chemistry, by Raymond Chang

Comparison of Electrochemical (Part 1) and Electrolytic cell (Part 2)

	ELECTROCHEMICAL CELL	**ELECTROLYTIC CELL**
		
Energy change	**chemical** energy → **electrical** energy	**electrical** energy → **chemical** energy
Cell Reaction	**Spontaneous** Chemical reaction takes place to generate electric current within celll (battery).	**Non-spontaneous** **External** electric current is applied to drive the reaction to occur.
Cathode (reduction)	**Positive (+) electrode**	**Negative (–) electrode**
Anode (oxidation)	**Negative (–) electrode**	**Positive (+) electrode**

Note:

1. In both electrochemical and electrolytic cells, **oxidation** always takes place at the **anode** while **reduction** always takes place at the **cathode**.

2. Polarity of electrode **always follow the polarity of the battery**.

   [ElectroCHEMICAL cell] The two half-cells form the battery.
   Anode is the negative terminal of the battery that releases electrons while cathode is the positive terminal of the battery that accepts electrons.

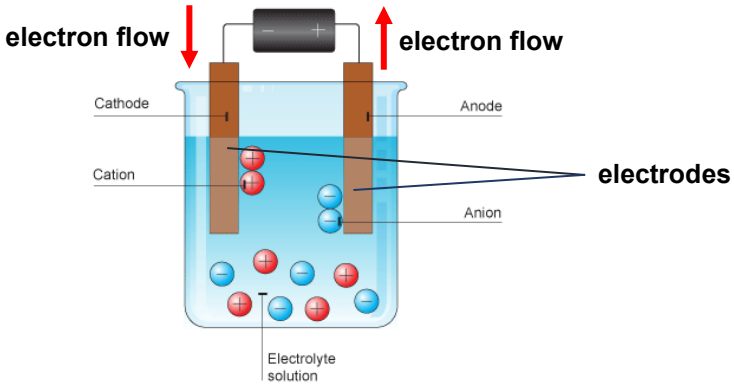
   [**ElectroLYTIC cell]** The ***polarities of the electrode are reversed***, as the electrodes follows the polarity of the battery terminal it is connected to.
   - **anode (+ve)** is connected to the +ve terminal of battery and **attracts anions** (−ve)
   - **cathode (−ve)** is connected to the –ve terminal of battery and **attracts cations** (+ve)

1 The Electrolytic Cell

Electrolysis is the process in which **electrical** energy is used to cause a **NON-spontaneous redox reaction** to occur.

Success Criteria:
- I can draw the set-up of an electrolytic cell to illustrate what constitutes the cell.
- I can identify the reduction or oxidation taking place at each electrode based on the polarity of the electrodes in the electrolytic cell.
- I can explain the differences between electrochemical and electrolytic cells in terms of energy change, spontaneity of the cell reaction and sign of the cathode and anode.

The set-up



An electrolytic cell is a container that consists of a **pair of electrodes** dipped in **an electrolyte** and connected to an **external source of electromotive force** (the battery).

Pause and ponder
Which half-reaction occurs in which electrode?
***An*ode, *Ox*idation;**

***Red*uction, *Cat*hode**

Useful aid:
(**An O**x, **Red C**at)

I. **The battery** drives electrons out of one electrode (**anode**) and into the other electrode (**cathode**), providing the driving force for the non-spontaneous chemical reaction to occur.

II. **Electrodes (Polarity of electrode <u>follows the polarity of the battery terminal it is connected to</u>)**

	chemical process	**polarity**
Cathode	reduction (gain of electrons)	Negative (gain e^- from -ve terminal of battery)
Anode	oxidation (loss of electrons)	Positive (Release e^- to +ve terminal of battery)

III. **An electrolyte** is a liquid or an aqueous solution, that contains **mobile ions** and conducts electricity.

The electrolyte could either be:

- a **molten liquid of ionic salt** (e.g. molten $PbBr_2$), or
- an **aqueous solution** containing ions (e.g. aqueous $CuSO_4$ or dilute H_2SO_4).

1.1 Electrolysis of Molten Salts

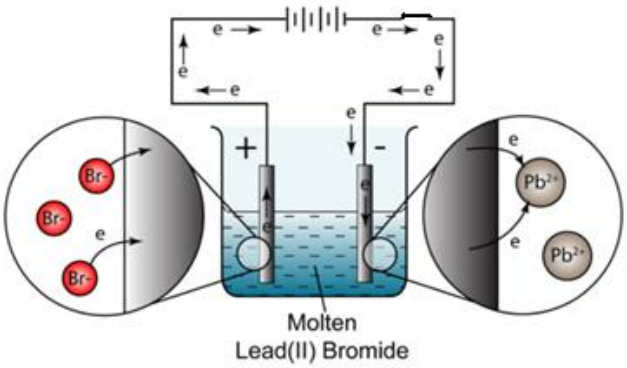
Success Criteria

- I can predict the products formed at each electrode (cathode and anode) for the electrolysis of molten salts by identifying the ions present in the electrolyte.

Some ionic salts, when molten, can be decomposed into their constituent elements by using electrical energy.

Worked Example 1

Consider the electrolysis of molten lead(II) bromide using inert platinum electrodes.



a) What are the ions present in the electrolyte?

Pb^{2+} and Br^-

b) What happens to these ions when the setup is connected to a battery?

Pb^{2+} ions (cation) move towards the cathode (-ve)
Br^- ions (anion) move towards the anode (+ve)

Useful aid:

Oxidation Is Loss of e^-

Reduction Is Gain of e^-

c) What chemical processes happen at the following electrodes? Write equations for the reactions that occur.

(i) Cathode **(attracts cations)**

Chemical process: **reduction**
Equation: **[R] $Pb^{2+} + 2e^- \longrightarrow Pb$**

(ii) Anode **(attracts anions)**

Chemical process: **oxidation**
Equation: **[O] $2Br^- \longrightarrow Br_2 + 2e^-$**

d) Deduce what would be observed at each of the electrodes after some time.

Cathode: **small beads of molten lead formed**
Anode: **brown fumes of bromine evolved**

Note: During electrolysis, cations receive electrons from the cathode while anions give up electrons to the anode. This process of gaining or losing electrons at the electrodes is termed as ***discharge***.

1.2 Electrolysis of Aqueous Solutions

Success Criteria

- I can predict the products formed in the electrolysis of aqueous solutions by identifying the ions/species with more positive $E^{\ominus}$ values at the cathode (–) electrode.
- I can predict the products formed in the electrolysis of aqueous solutions by identifying the ions/species with less positive (more negative) $E^{\ominus}$ values at the anode (+) electrode.

In the electrolysis of aqueous solutions, the ions/species which need to be considered for discharge are:

- water
- cations and anions (possibly mixtures)

Only **one** ion/ species is discharged at an electrode at any one time. This is called ***selective discharge*** of species.

The **factors** that affect the selective discharge of ions/species at each electrode are:

- position of the ions in the electrochemical series (their relative $E^{\ominus}$ values)
- concentration of the ions
- nature of the electrode

1.2.1 Relative electrode potential

	chemical process	species discharged	electrode potential, $E^{\ominus}$
Cathode (−ve)	**reduction**	species that is more easily reduced (Compare cations and H_2O)	More positive $E^{\ominus}$
Anode (+ve)	**oxidation**	species that is more easily oxidised (Compare anions and H_2O)	Less positive $E^{\ominus}$

Reduction takes place for the species with ***more positive*** $E^{\ominus}$ va*lues* ($E^{\ominus}$ measures the tendency for reduction to take place).

For electrolysis of an aqueous solution, at the cathode, metal cations such as Cu^{2+} and Ag^{+} would be reduced since their $E^{\ominus}$ **values are more positive than** $E^{\ominus}$ **(H_2O/H_2)** and they are **more readily reduced** than H_2O.

$Cu^{2+} + 2e^{-} \rightleftharpoons Cu$ $\quad E^{\ominus} = +0.34$ V

$Ag^{+} + e^{-} \rightleftharpoons Ag$ $\quad E^{\ominus} = +0.80$ V

$2H_2O + 2e^{-} \rightleftharpoons H_2 + 2OH^{-}$ $\quad E^{\ominus} = -0.83$ V

Worked Example 2

Using information from the *Data Booklet*, predict the reactions that would take place at the **cathode** and **anode**, when each of the solution is electrolysed.

a) aqueous solution containing $Cu(NO_3)_2$ and $AgNO_3$

Species present: Cu^{2+}, Ag^+, NO_3^-, H_2O

At **cathode** (**reduction**): **Species present: Cu^{2+}, Ag^+, H_2O**

	$E^\ominus$ / V
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	–0.83

Ag^+ is reduced to **Ag** as it has the **most positive** reduction potential.
[R] $Ag^+ + e^- \longrightarrow Ag$

Note:
NO_3^- ions are not oxidised (N of NO_3^- is in its maximum possible oxidation state of +5 and thus cannot be oxidised)

At **anode** (**oxidation**): **Species present: NO_3^-, H_2O**

	$E^\ominus$ / V
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23

H_2O is oxidised to **O_2**.
[O] $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

b) a solution of $CaCl_2$ in dilute nitric acid

Species present: Ca^{2+}, H^+, Cl^-, NO_3^-, H_2O

At **cathode** (**reduction**): **Species to consider: Ca^{2+}, H^+, H_2O**

	$E^\ominus$ / V
$Ca^{2+} + 2e^- \rightleftharpoons Ca$	–2.87
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	−0.83

H^+ is reduced to H_2 as it has the **most positive** reduction potential.
[R] $2H^+ + 2e^- \longrightarrow H_2$

Note:
NO_3^- cannot be oxidised

At **anode** (**oxidation**): **Species to consider: Cl^-, NO_3^-, H_2O**

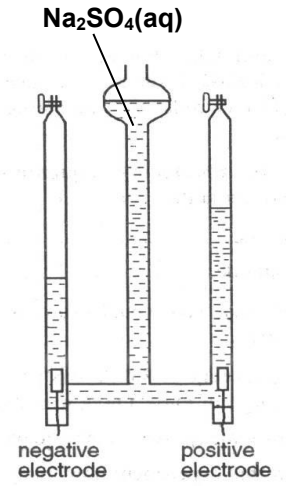
	$E^\ominus$ / V
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23

H_2O is oxidised to O_2, as it has a **less positive** $E^\ominus$ value, while **Cl^-** remains in the solution.
[O] $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

Checkpoint 1 [J97/2/3 (modified)]

1. The electrolysis of aqueous sodium sulfate containing litmus indicator was carried out in the apparatus shown below using inert electrodes. After some time, the volumes of gases liberated were as shown in the diagram. The litmus in both electrode compartments also changed colour.

(a) Using data from the *Data Booklet*, consider which species will be preferentially discharged, write the appropriate ion-electron half-equations, for the changes which take place in each electrode compartment.



Species present:

At **cathode ( )**:
Species to consider:

	$E^{\ominus}$ / V
$\underline{Na^+} + e^- \rightleftharpoons Na$	–2.71
$2\underline{H_2O} + 2e^- \rightleftharpoons H_2 + 2OH^-$	–0.83

Reaction at <u>cathode</u>:
[R]:

At **anode ( )**:
Species to consider:

	$E^{\ominus}$ / V
$O_2 + 4H^+ + 4e^- \rightleftharpoons \underline{2H_2O}$	+1.23
$S_2O_8^{2-} + 2e^- \rightleftharpoons \underline{2SO_4^{2-}}$	+2.01

Reaction at <u>anode</u>:
[O]:

(b) Hence explain why the gas volumes are in the ratio 2 : 1.

During electrolysis, same amount of charges pass through the anode and cathode. For every **<u>4</u>** mol of electrons passed, _____mol of H_2 and ____mol of O_2 are produced at the cathode and anode respectively. Hence, ratio of the volumes of $H_2(g)$: $O_2(g)$ is _____.

(c) State and explain the colour of the litmus around each electrode.

At the negative electrode (cathode), _____ions are produced. Thus, litmus turns _____around this electrode.

At the positive electrode (anode), _____ions are produced. Thus, litmus turns _____around this electrode.

1.2.2 Concentration of ions

Success Criteria:

- I can state and explain why chlorine gas is discharged preferentially in the electrolysis of concentrated NaC*l* by relating how higher concentration of C*l*$^-$ would result in less positive $E(Cl_2/Cl^-)$ using Le Chatelier's principle.

Ions, which are **present in high concentrations**, may be **discharged preferentially** even though its position in the electrochemical series may suggest otherwise.

Concentration factor can only override prediction (using electrode potential) provided that the difference between the competing $E^\ominus$ values is small.

Compare the products of the following electrolytic processes using inert electrodes:

Note:
For A level H2 Chemistry, preferential discharge of C*l*$^-$ at high concentration is commonly asked in examinations.

Electrolyte	Products at cathode	Products at anode
dilute NaC*l*	H_2 and OH^-	O_2 and H^+
concentrated NaC*l* (**brine**)	H_2 and OH^-	Cl_2

Pause and ponder

a) Are the products at the cathode expected? Why?

Species to consider: Na^+, H_2O

	$E^\ominus$ / V
$Na^+ + e^- \rightleftharpoons Na$	–2.71
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	–0.83

Yes, $E^\ominus(H_2O/H_2) = -0.83$ V is much more positive than $E^\ominus(Na^+/Na) = -2.71$.

Thus, the reduction of **H_2O** to **H_2** is favoured.

b) Are the products at the anode what you would expect? Suggest a reason for the observation.

Species to consider: Cl^-, H_2O

	$E^\ominus$ / V
$O_2 + 4H^+ + 4e^- \rightleftharpoons \underline{2H_2O}$	**+1.23**
$Cl_2 + 2e^- \rightleftharpoons \underline{2Cl^-}$	**+1.36**

Dilute NaCl – **expected** since $E^\ominus(O_2/H_2O) = +1.23$ V **<** $E^\ominus(Cl_2/Cl^-) = +1.36$ V
Thus, the oxidation of **H_2O** to **O_2 and H^+** is favoured.

Conc. NaCl – **unexpected**
Reason: high $[Cl^-]$ in solution causes $E(Cl_2/Cl^-)$ to become less positive.

For the equilibrium: $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$

The position of equilibrium would shift to the **left** due to high $[Cl^-]$ (Le Chatelier's Principle); causing $E(Cl_2/Cl^-)$ to **decrease to less positive** than +1.23 V [$E^\ominus(O_2/H_2O)$].

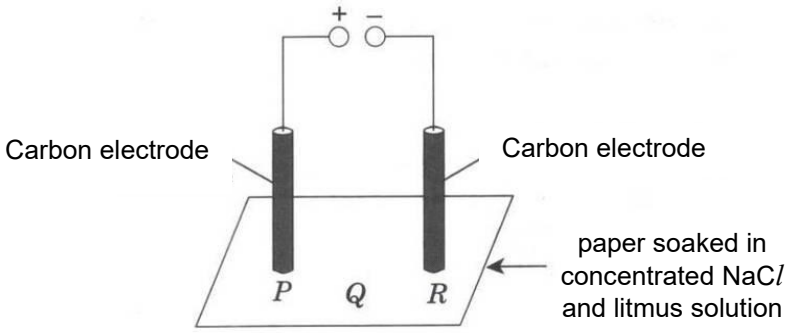
Hence, Cl^- *is* ***preferentially oxidised*** and Cl_2 is produced.

Pause and ponder:
What would happen to the electrolyte in the solution over time?

	Overall equation for reaction	**Effect on electrolyte**
Dilute NaCl	$2H_2O \longrightarrow 2H_2 + O_2$	NaCl (aq) becomes more concentrated as water undergoes reduction at the cathode and oxidation at the anode.
Concentrated NaCl (brine)	$2Cl^- + 2H_2O \longrightarrow Cl_2 + H_2 + 2OH^-$	Electrolyte becomes basic eventually due to the formation of $OH^-(aq)$.

Checkpoint 2

A current is passed through the apparatus set up as shown below.



Which of the following colours would be expected to appear on the paper at the points, *P* and *R*?

	P	***R***
A	white	blue
B	red	blue
C	blue	red
D	blue	white

1.2.3 Nature of electrodes

Success Criteria:
- I can predict the reaction taking place at each electrode by considering the $E^{\ominus}$ values of the species/reactive electrode present.

Note:
Inert electrode (e.g., Pt, graphite) **will not participate** in the electrolysis reaction

Reactive electrode (e.g., Cu anode) could be **oxidised at the anode during electrolysis**

a) Inert electrodes

These are electrodes that do not undergo oxidation during electrolysis, e.g., platinum and graphite (carbon) electrodes.

***Note*:** CO and CO_2 may be formed at graphite electrodes if O_2 is produced, especially at high temperatures. The graphite electrodes will undergo combustion reaction with the hot $O_2(g)$ and must be replaced regularly.

b) Reactive electrodes

These are electrodes that may undergo oxidation at the anode during electrolysis.

Consider electrolysis of $CuSO_4(aq)$:

	Pt/Graphite electrodes	**Copper electrodes**
Species present	**Cu^{2+}, SO_4^{2-}, H_2O**	**Cu^{2+}, SO_4^{2-}, H_2O, Cu**
Reaction at **anode** [Preference for oxidation: - **less positive $E^{\ominus}$**]	Relevant electrode potentials: $S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ +2.01 V $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ +1.23 V H_2O is oxidised in preference over SO_4^{2-} **[O]: $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$**	Relevant electrode potentials: $S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ +2.01 V $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ +1.23 V $Cu^{2+} + 2e^- \rightleftharpoons Cu$ +0.34 V Cu atoms of Cu electrode are oxidised to Cu^{2+} in preference over SO_4^{2-} and H_2O. **[O]: $Cu \longrightarrow Cu^{2+} + 2e^-$**
Reaction at **cathode** [Preference for reduction: - **more positive $E^{\ominus}$**]	Relevant electrode potentials: $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ –0.83 V $Cu^{2+} + 2e^- \rightleftharpoons Cu$ +0.34 V **Cu^{2+} is reduced** in preference over H_2O. **[R]: $Cu^{2+} + 2e^- \longrightarrow Cu$**	Relevant electrode potentials: $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ –0.83 V $Cu^{2+} + 2e^- \rightleftharpoons Cu$ +0.34 V **Cu^{2+} is reduced** in preference over H_2O. **[R]: $Cu^{2+} + 2e^- \longrightarrow Cu$**
Observation	**Cathode:** Pink Cu(s) is deposited. **Anode:** Effervescence of $O_2(g)$ seen. **Electrolyte:** Intensity of blue colour decreases (due to decrease in $[Cu^{2+}]$)	**Cathode:** Pink Cu(s) is deposited. **Anode:** Cu(s) anode dissolves. **Electrolyte:** intensity of blue colour remains unchanged

Checkpoint 3 

Predict the reactions that occur at each electrode when the following molten salts and aqueous solutions are electrolysed.

a) Using **graphite** electrodes

i) Molten $BaCl_2$ (Species present:)

Relevant $E^{\ominus}$/ V at cathode (cation)	Relevant $E^{\ominus}$/ V at anode (anion)
Reaction at cathode **[R]**	Reaction at anode **[O]**

ii) Dilute NaOH (Species present:)

Relevant $E^{\ominus}$/ V at cathode (cation, H_2O)	Relevant $E^{\ominus}$/ V at anode (anion, H_2O)
Reaction at cathode **[R]**	Reaction at anode **[O]**

iii) $AgNO_3$ (aq) (Species present:)

Relevant $E^{\ominus}$/ V at cathode (cation, H_2O)	Relevant $E^{\ominus}$/ V at anode (anion, H_2O)
Reaction at cathode **[R]**	Reaction at anode **[O]**

(b) H_2SO_4 (aq) using **Cu electrodes** (Species present: H^+, SO_4^{2-}, H_2O, Cu)

Relevant $E^{\ominus}$/ V at cathode (cation, H_2O)	Relevant $E^{\ominus}$/ V at anode (anion, H_2O,Cu)
Reaction at cathode **[R]**	Reaction at anode **[O]**

2 Quantitative Electrolysis

Success Criteria:

- I can identify and write the electrolysis half equation at each electrode.
- I can use the formula $F = L \times e$, $Q = \eta_e \times F$ and $Q = I \times t$, and experimental data to
  - determine the experimental value of Faraday's or Avogadro's constant
  - calculate the moles of electrons, η_e, provided by the current and time taken
- I can use the moles of electrons, η_e, transferred to determine the amount of substance (oxidized, reduced, or discharged) using the stoichiometry ratio of the half equation.

2.1 Definitions and relationship between Faraday's constant, *F*, Avogadro's constant, *L*, and electronic charge, *e*

Note:
From the Data Booklet,
$F = 96500$ C mol^{-1}
$L = 6.02 \times 10^{23}$ mol^{-1}
$e = 1.60 \times 10^{-19}$ C

- **Faraday's constant**, ***F***, is the amount of charges carried by **1 mol** of **electrons** that flowed through a cell.
- **Avogadro constant**, ***L***, is the number of particles in **1 mol** of such particles.
- **Electronic charge, e**, is the charge on an electron.
- The relationship between Faraday's constant, ***F***, Avogadro constant, ***L*** and the charge on an electron, ***e***, can be expressed as:

$$F = L \times e$$

2.2 Quantity of charge, *Q*, passed during electrolysis

Faraday's law of electrolysis: the **number of moles of a substance** that undergoes oxidation or reduction at each electrode during electrolysis is **directly proportional to the quantity of charge** that passes through the cell.

- The relationship between the total **quantity of charge**, ***Q***, carried by electrons that are transferred in the cell during electrolysis can be expressed as:

$$Q = \eta_e \times F$$

where η_e = **amount (mol) of electrons** transferred in the cell.

Note:
Units of
Q is **C** (Coulombs)
I is **A** (Amperes)
t is **s** (Seconds)

- During electrolysis, this **quantity of charge, *Q*,** can be produced by passing a fixed current, ***I***, over time, **t**, through the cell. The relationship can be expressed as:

$$Q = I \times t$$

- In summary, we can combine the two formulas:

$$\eta_e \times F = I \times t$$

2.3 The mass or volume of substance liberated during electrolysis

Using Faraday's law and the equations above, the amount of product liberated can be determined.

Worked Example 3

A current of 2 A was passed through silver nitrate solution for 32 min and 10 s. Calculate the mass of silver discharged at the cathode. (A_r: Ag = 107.9)

At cathode: **[R]** $Ag^+ + e^- \longrightarrow Ag$

$\mathbf{I \times t = \eta_e \times F}$

Note:
Unit for t is "seconds"

$\eta_e = \frac{I \times t}{F} = \frac{2 \times (32 \times 60 + 10)}{96500} = 0.0400$ mol

amount of Ag formed = 0.0400 mol

Mass of silver formed = $0.0400 \times 107.9 = \underline{4.32\ g}$

Worked Example 4

A current was passed through dilute sulfuric acid for 30 minutes. Calculate the magnitude of current when 0.244 dm^3 of oxygen gas (measured at room temperature and pressure) is liberated at the anode.

At anode: **[O]** $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

Amt of $O_2 = \frac{0.244}{24} = 1.017 \times 10^{-2}$ mol

$\eta_e = 4 \times 1.017 \times 10^{-2} = 4.067 \times 10^{-2}$ mol

Note:
Unit for t is "seconds"

$\mathbf{I \times t = \eta_e \times F}$

$\mathbf{I} = \frac{4.067 \times 10^{-2} \times 96500}{(30 \times 60)} = \underline{2.18\ A}$

Checkpoint 4

A layer of chromium is electroplated on an automobile bumper by passing a constant current of 200 A through a cell that contains $Cr^{3+}(aq)$. Calculate the time taken in minutes to deposit 125 g of chromium. (A_r: Cr = 52.0)

(Time taken = 58.0 min)

Worked Example 5

When a current of 3.0 A was passed for 30 minutes through molten lead(II) bromide in an evaporating basin using graphite electrodes, a bead of lead of mass 5.60 g was obtained.

Note:
Unit for t is "seconds"

(a) Calculate the amount of charge that was passed.

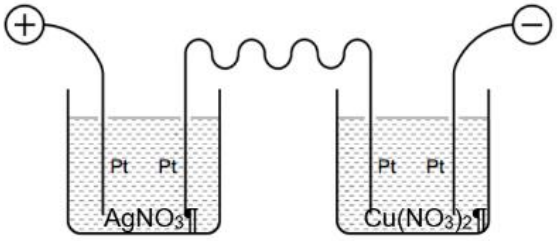
(b) Calculate the value of F from this experiment data.

(c) Using the value of *e* (charge on an electron) from the *Data Booklet*, determine the value of Avogadro's number as determined from this experiment.

(d) Suggest a reason, in terms of the experimental set-up, why the value obtained in **(c)** is not exactly the theoretical value?

Worked Example 6

An electrolytic cell containing silver nitrate and an electrolytic cell of copper nitrate, both using inert electrodes, are connected in series to a battery.



Calculate the ratio of number of moles of silver to number of moles of copper deposited at the respective electrode.

Since the cells are connected in series, the quantity of charge passed is the same for both cells.

Reduction at each cathode:

[R] $Ag^+ + e^- \longrightarrow Ag$ **[R] $Cu^{2+} + 2e^- \longrightarrow Cu$**

Amount of Ag deposited per mole of electrons passed = 1 mol

Amount of Cu deposited per mole of electrons passed = 0.5 mol

∴ Amount of silver deposited: Amount of copper deposited
= 1 : 0.5
= 2 : 1

Checkpoint 5

In an electrolytic experiment, 1 mol dm^{-3} aqueous silver nitrate was used as the electrolyte. After some time, ***m*** g of silver was deposited.

The experiment was repeated for the same duration at the same current, but with 2 mol dm^{-3} solution of silver nitrate. What was the mass of silver deposited? Why?

3 Practical Applications of Electrolysis

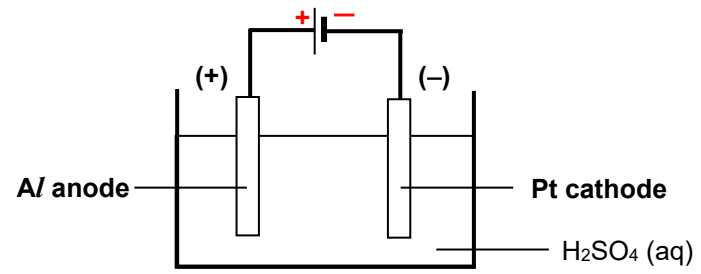
3.1 Anodising of aluminium - to **<u>increase the thickness</u>** of Al_2O_3 protective layer on the surface of Al metal by electrolysis

Success Criteria:
- I can describe the process of anodising of aluminum with an electrolytic cell diagram drawn and write the half equation of the reaction at each electrode.

- Aluminium is a reactive metal and can be oxidised easily. However, aluminium metal objects are usually resistant to corrosion because when exposed to air, aluminium forms a layer of Al_2O_3 on its surface. This impervious oxide layer is resistant to corrosion, and it acts as a protective layer which seals off the aluminium beneath it from further reaction.

- **Anodising** is a surface treatment to **<u>increase the thickness</u>** of the corrosion resistant $Al_2O_3(s)$ layer on the surface of aluminium metal by electrolysis.

- During anodising, the aluminium object is made the **anode**.



Electrolyte: **$H_2SO_4(aq)$**
Electrodes: **Al anode, Pt cathode**

Reaction at the anode: **[O]: $2Al + 3H_2O \longrightarrow Al_2O_3 + 6H^+ + 6e^-$**
(Oxidation of Al to Al_2O_3 in acidic medium, balance the half equation)

Reaction at the cathode: **[R]: $2H^+ + 2e^- \longrightarrow H_2$**

- **Advantages**:
  - increase corrosion resistance of the metal
  - provide a porous surface which can be dyed to different colours. If a dye is added in the process, it can be adsorbed on the oxide layer.

- **Uses**:
  Materials for window frames, drink cans and casing for hand phones etc.

Note:
2 reactions occur at anode to produce Al_2O_3.
Rxn 1: Oxidation of H_2O produces O_2,
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

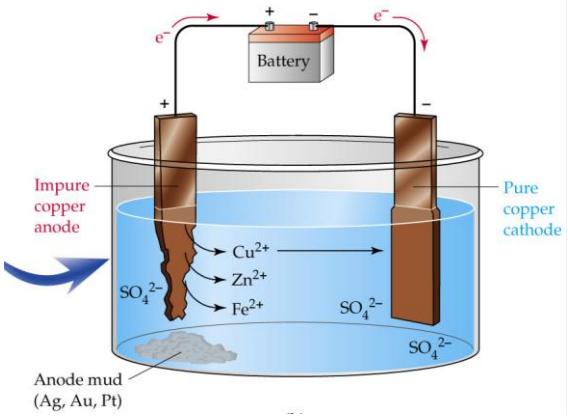
Rxn 2: Hot O_2 from **Rxn 1** reacts with Al to give Al_2O_3.
$2Al + 3/2O_2 \rightarrow Al_2O_3$

3.2 Purification of Copper

Success Criteria:

- I can describe the process of purification of copper with an electrolytic cell diagram drawn.
- I can write and explain the half equations of the reactions taking place at each electrode based on the $E^{\ominus}$ values of the species/reactive electrode present.

- Impure copper is purified by electrolysis. The impure copper is made the **anode** and a piece of pure copper is made the **cathode**.



Anode: **Impure copper (containing traces of Zn, Fe, Ag, Au)**
Cathode: **Pure copper**
Electrolyte: **Dilute $CuSO_4$(aq)**
Species present: **Cu^{2+}, SO_4^{2-}, H_2O, Cu, Zn, Fe, Ag, Au**

a) At the **anode**, Zn, Fe and Cu is oxidised to their respective ions, thus dissolving into the electrolyte.

$$\textbf{[O] Zn} \longrightarrow \textbf{Zn}^{2+} + \textbf{2e}^{-}$$
$$\textbf{[O] Fe} \longrightarrow \textbf{Fe}^{2+} + \textbf{2e}^{-}$$
$$\textbf{[O] Cu} \longrightarrow \textbf{Cu}^{2+} + \textbf{2e}^{-}$$

b) At the **cathode**, the Cu^{2+} ions present in the electrolyte are reduced to Cu(s), depositing onto the cathode.

$$\textbf{[R] Cu}^{2+} + \textbf{2e}^{-} \longrightarrow \textbf{Cu}$$

Metal impurities in copper ore

	$E^{\ominus}$/ V
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.76
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0.44
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$Ag^{+} + e^- \rightleftharpoons Ag$	+0.80
$Au^{+} + e^- \rightleftharpoons Au$	+1.69

1. Metals impurities with **less positive** electrode potentials than Cu, such as Zn and Fe, are **more readily oxidised** than Cu at the **anode** before Cu and they dissolve into the electrolyte as ions.

The Zn^{2+} and Fe^{2+} ions formed will remain in the electrolyte and not be reduced at the cathode, as they have a lower tendency to be reduced than Cu^{2+}.

2. Metal impurities with **more positive** electrode potentials than Cu, such as Ag and Au, are **not oxidised** as they have a lower tendency to be oxidised than Cu. They are collected below the anode as "***anode sludge***".

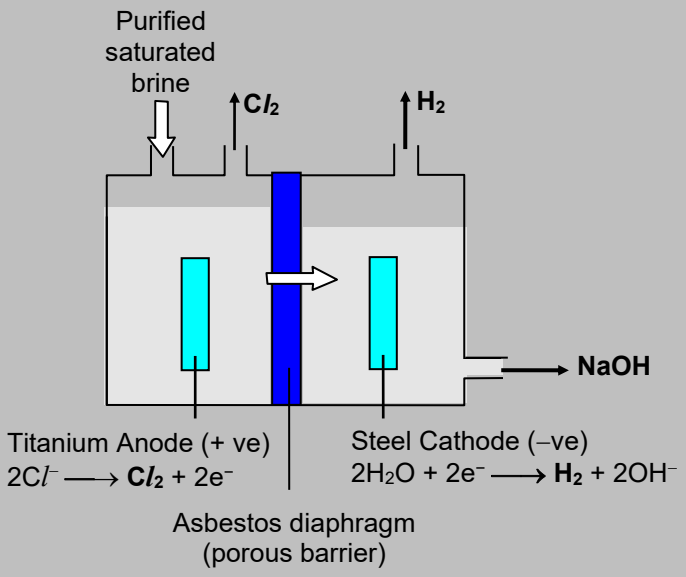
Checkpoint 6

Which treatment is frequently used to protect aluminium articles from subsequent corrosion?

A making the aluminium the anode during an electrolysis
B dipping the aluminium in hot aqueous sodium hydroxide
C dipping the aluminium in molten cryolite (Na_3AlF_6)
D attaching a less reactive metal to the aluminium

Use of Electrolysis in the Production of Chemicals *(For Your Information)*

Electrolysis of Brine (concentrated NaCl) using the Diaphragm Cell



Overall reaction:

$$2NaCl + 2H_2O \xrightarrow{\text{electrolysis}} 2NaOH(aq) + Cl_2(g) + H_2(g)$$

1. Titanium is used as the anode because it resists corrosion by the very reactive chlorine.

2. Mixtures of H_2 and Cl_2 are prevented from mixing as both are highly reactive when they come into contact, hence they are separated.

3. The level of the brine on the anode side of the cell is higher than on the cathode side so that the brine will slowly flow through the asbestos diaphragm towards the cathode, carrying the sodium ions with it. Back flow of sodium hydroxide towards the anode is also prevented so that it does not react with chlorine.

4. The initial products from the above process are chlorine, sodium hydroxide and hydrogen.

ELECTROLYTIC CELL TUTORIAL

Electrolysis of Molten or Aqueous Solution

1 Predict the products formed at the electrodes, when each of the following samples is electrolysed.

(a) molten copper(II) chloride using inert electrodes.

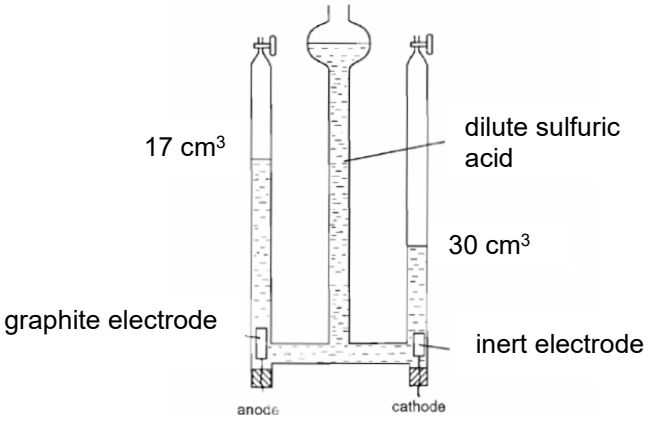
(b) aqueous copper(II) chloride using inert electrodes.

(c) concentrated copper(II) chloride using inert electrodes.

(d) aqueous copper(II) chloride using copper electrodes.

2 **(a)** Give the half equation for the electrode reactions in the electrolysis of aqueous sulfuric acid using inert electrodes.

(b) When a graphite anode is used in this electrolysis, the gas liberated is a mixture of oxygen, carbon monoxide and carbon dioxide. In the experiment illustrated, 30 cm^3 of gas formed above the cathode and 17 cm^3 of gas above the anode. The anode gas was collected and this volume was reduced to 9 cm^3 when shaken with aqueous sodium hydroxide.



(i) Calculate the volume of oxygen would you expect to be produced at the anode using an inert electrode.

(ii) Explain why oxides of carbon are produced at the anode.

(iii) The volume of gas collected at the anode is larger than that expected. Explain, with the aid of an equation, why this is so.

(iv) Calculate volume of carbon dioxide was present in the 17 cm^3 of gas from the anode.

(v) Considering your answers from **(i), (iii), (iv)**, calculate the volume of carbon monoxide and oxygen in the anode respectively.

Quantitative Electrolysis

3 Which option correctly list the factors that determine the number of atoms of copper deposited on the cathode of an electrolytic cell?

	$[Cu^{2+}$ (aq)]	*current*	*time*
A	✓	×	×
B	×	✓	✓
C	✓	✓	×
D	×	×	✓

4 During electrolysis under suitable conditions, 0.015 mol of chromium is deposited at the cathode when 0.090 mol of electrons is passed through a chromium-containing electrolyte.

What is the oxidation state of Cr in the electrolyte?

A +3 **B** +4 **C** +5 **D** +6

5 **[2021/P1/Q27]** In the electrolysis of molten aluminium oxide, 0.27g of aluminium is liberated when 2904 coulombs of electricity is passed through molten aluminium oxide.

Which value of Avogadro's constant do **these figures** give?

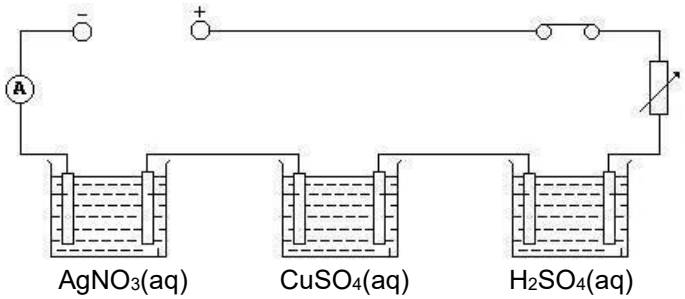
A 6.02×10^{23} **B** 6.05×10^{23} **C** 1.82×10^{24} **D** 2.02×10^{23}

6 A current was passed through molten aluminium oxide. The volume of oxygen collected at the anode was **113.5 cm^3** measured at s.t.p. What is the mass of aluminium obtained at the cathode?

A 0.810 g **B** 0.180 g **C** 0.027 g **D** 0.09 g

Answer key for MCQ:
3) B 4) D 5) B 6) B

7 Using platinum electrodes, a current of 2.5 A was passed through three beakers containing, respectively, aqueous silver nitrate, aqueous copper(II) sulfate and dilute sulfuric acid, connected in series. 0.40 g of silver was deposited in the first beaker.



(a) Calculate the mass of copper deposited in the second beaker.

(b) Calculate the volume of hydrogen liberated at 17 °C and 1 atm in the third beaker, and the length of time the current was passed.

8 **Modified from J00/I/4(c)**

When an iron sheet is made the anode during the electrolysis of very concentrated aqueous potassium hydroxide, an anion containing iron in a high oxidation state is formed in solution. The addition of an excess of barium nitrate to this solution precipitates a red solid having the chemical formula $BaFeO_4$

(i) Calculate the oxidation number of iron in $BaFeO_4$.

(ii) After a current has been passed through the solution for some time, the addition of barium nitrate produces 1.00 g of the red solid. Calculate how many moles of red solid are formed, and hence calculate how many coulombs of electricity were needed.

Application Questions

9 Fluorine gas can be manufactured by the electrolysis of molten potassium fluoride.

(a) Calculate the time needed (in hours) to electrolyse 500 kg of potassium fluoride completely, using a current of 1.20×10^5 A.

(b) Unlike fluorine, chlorine can be obtained by the electrolysis of concentrated KC*l*. Electrolysis of concentrated KF produces only oxygen gas at the anode.

Use relevant $E^{\ominus}$ data from the *Data Booklet* to explain these observations.

10 Over one million tonnes of chromium are produced in the world each year and about 30% of it is used in electroplating. In an electroplating experiment, an aqueous solution containing chromium(III) sulfate was electrolysed using a piece of pure chromium and the metal object to be electroplated as the electrodes.

(a) A current was passed for 1.5 hours and the mass of the metal object was found to increase by 3.7 g. Calculate the current used.

(b) An attempt to coat another object with aluminium was made by repeating the experiment in **(a)** but using aqueous aluminium sulfate instead of chromium(III) sulfate and a piece of pure aluminum instead of pure chromium. Do you expect the experiment to be successful? Give reasons to support your answer.

11 **(a)** **[N14/3/5]** When a particular copper ore was reduced, an alloy was produced which was composed mainly of copper, but with nickel and silver as minor impurities. It contained no other metal. In order to purify it, this alloy was made the anode of an electrolysis cell, with a pure copper cathode and aqueous $CuSO_4$ as electrolyte.

Explain, with reference to relevant $E^{\ominus}$ values, what happens to the nickel and silver impurities during this purification procedure.

(b) A current of 2.00 A was passed through the cell described in **(a)** for 23.0 minutes, and the electrodes removed, washed, dried and weighed. It was found that the anode had lost 0.950 g.

After filtering it off and drying it, the deposit underneath the anode weighed 0.0500 g.

On adding an excess of dimethylglyoxime to the electrolyte, the highly insoluble red complex with the formula $Ni(C_4H_7N_2O_2)_2$ was precipitated, its mass was 0.492 g.

(i) Calculate the expected increase in mass of the cathode.

(ii) Calculate the actual masses of copper, nickel and silver removed from the alloy.