RAFFLES INSTITUTION
YEAR 6 H2 CHEMISTRY 2023
Lecture Notes 21b – Electrochemistry 2 (Electrolysis)

A Content

Electrolysis

(i) Factors affecting the amount of substance liberated during electrolysis
(ii) Industrial uses of electrolysis
(iii) The Faraday constant; the Avogadro constant; their relationship

B Learning outcomes

Candidates should be able to:

(a) state the relationship, $F = Le$, between the Faraday constant, the Avogadro constant and the charge on the electron
(b) 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
(c) calculate:
    (i) the quantity of charge passed during electrolysis
    (ii) the mass and/or volume of substance liberated during electrolysis
(d) 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]

C References

1. Chemistry for Advanced Level by Peter Cann and Peter Hughes
2. Chemistry the Central Science by T L Brown and H E Lemay
3. Chemistry by Zumdahl

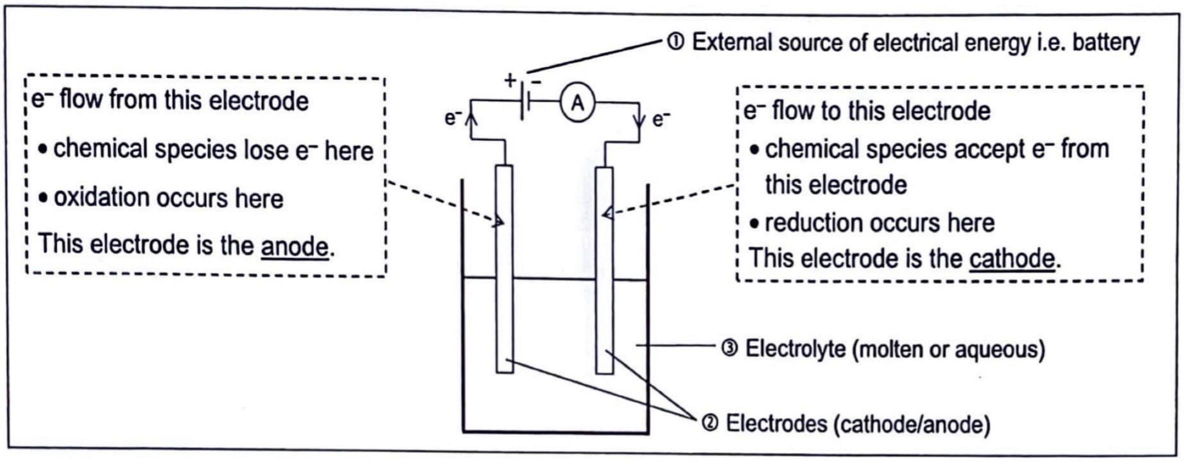
D Online Resources

1. http://www.chemguide.co.uk/physical/redoxeqiamenu.html#top

1 INTRODUCTION

1.1 Basic set up

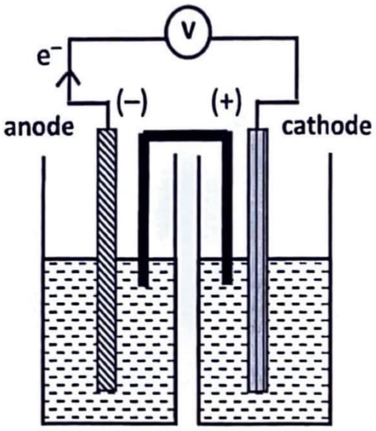
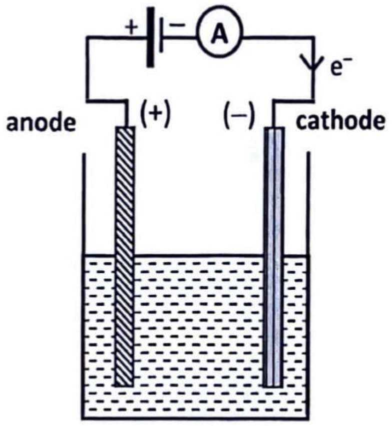
- The process of passing **electricity (from an external source)** to force a **non–spontaneous** redox reaction to occur is called **electrolysis**.
- The cell in which electrolysis occurs is called the **electrolytic cell**.
- A typical electrolytic cell has the following components:

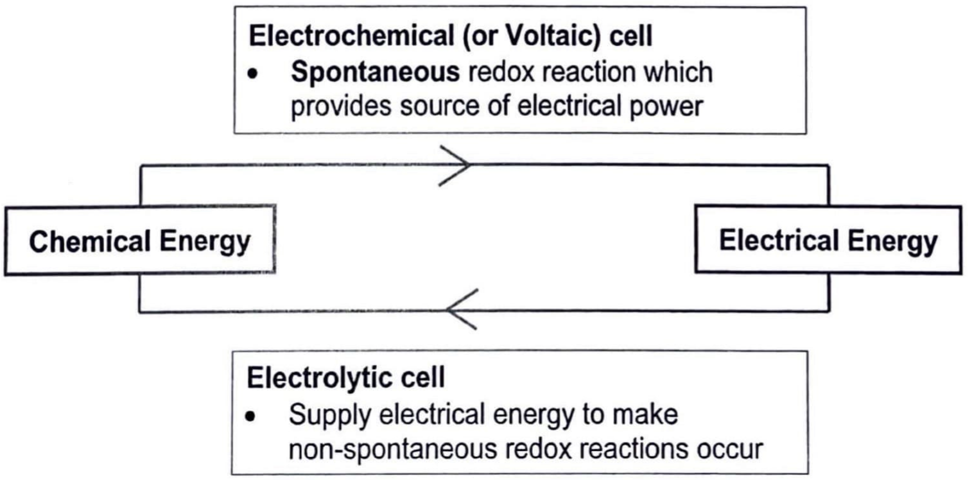


- During electrolysis, there are two possibilities for "chemical change":
  a) electrolyte – its components are oxidised or reduced.
  b) electrode – a Reactive anode is oxidised.
- Due to the redox processes occurring, some possible physical observations are:
  a) the electrolyte changes colour or colour intensity,
  b) bubbling at the cathode or anode (i.e. a gas is evolved),
  c) a solid metal deposits on the cathode,
  d) the anode decreases in size and mass (i.e. it dissolves).

Note:
- Substances are described as being *liberated* (for substances produced) or *discharged* (for species that underwent redox reaction) during electrolysis.
- Any oxidation always takes place at the anode.
- Any reduction always takes place at the cathode.

1.2 Comparison between Electrochemical (or Voltaic) Cell & Electrolytic Cell

Type of Cell	Electrochemical (or Voltaic) Cell		Electrolytic Cell	
Diagram	<u>Spontaneous</u> redox reaction in cell produces electricity.  		Electricity from external source forces a Non-spontaneous redox reaction to occur.  	
Energy conversion	chemical → electrical energy		electrical → chemical energy	
External Source	No		Yes	
Salt Bridge	Usually Yes		No	
Electrode	Anode	Cathode	Anode	Cathode
Half-equation	Oxidation	Reduction	Oxidation	Reduction
Sign	–	+	+	–
Electron flow in external circuit	From anode to cathode		From anode to cathode	



Electrochemical (or Voltaic) cell
- **Spontaneous** redox reaction which provides source of electrical power

Electrolytic cell
- Supply electrical energy to make non-spontaneous redox reactions occur

Note: Unlike in electrochemical cells, we **<u>DO NOT</u>** consider $E^{\ominus}_{cell} > 0$ when setting up **electrolytic cells.** Non-spontaneous reactions are taking place instead, driven by an external power source. **Key considerations for choosing which reactions take place are discussed in section 2.**

Useful tip: the polarity of electrodes in electrolytic cells are opposite that of electrochemical cell. An easy way to remember this is the **cathode** forces **reduction** and provides **electrons** from the power source. Hence it is **negative**.

2 FACTORS AFFECTING SELECTIVE DISCHARGE OF IONS

Candidates should be able to 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.

When an electrical potential is applied across the two electrodes in an electrolytic cell, not all species present undergo simultaneous discharge.

In fact, the cation or anion that is discharged is the one that requires the least energy. This is called **selective/preferential discharge**.

The order in which ions are discharged at the electrodes are influenced by:

(A) the physical state of electrolyte (molten or aqueous); note that $E^\ominus$ values do not actually apply in molten states.

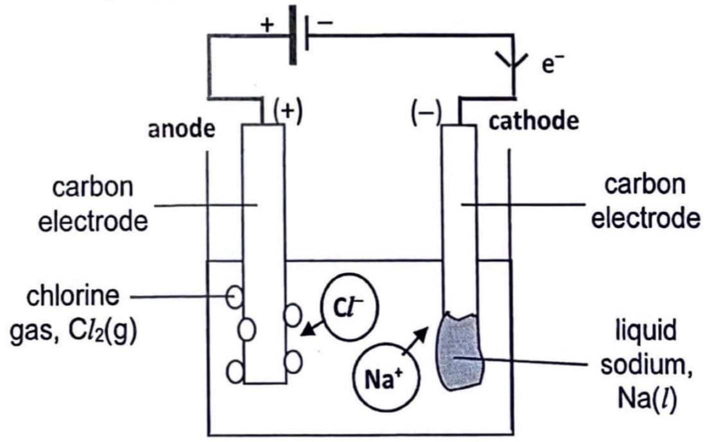
(B) electrode potential, $E^\ominus$,

(C) the relative concentration of the species,

(D) the nature of the electrodes (inert or reactive)

(A) Physical State of Electrolyte (Molten or Aqueous)

Compare the electrolysis of molten $NaCl(l)$ and dilute $NaCl(aq)$

molten $NaCl(l)$	**Species present in electrolyte**	$Na^+(l)$ and $Cl^-(l)$
	Electrodes	Inert electrodes e.g. graphite
	Cathode (–)	$Na^+(l)$ migrates to the **cathode** (negative electrode) and is discharged i.e. $Na^+(l)$ gains electrons is **reduced** to $Na(l)$. $Na^+(l) + e^- \rightarrow Na(l)$
	Anode (+)	Cl^- migrates to the **anode** (positive electrode) and is discharged, i.e. Cl^- loses electrons and is **oxidised** to Cl_2. $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$
	Overall equation	$2NaCl(l) \rightarrow 2Na(l) + Cl_2(g)$
	Setup	

Going into the next example, we will observe in aqueous dilute NaCl, the options for discharge are different, and selection criteria need to be applied.

(B) Electrode Potential

Recall: A **more positive** (or less negative) $E^\ominus$ implies a higher tendency for **reduction** to occur and conversely, a **less positive** (or more negative) $E^\ominus$ implies a higher tendency for **oxidation** to occur.

Dilute aqueous NaC*l*	**Species present in electrolyte**	$Na^+(aq)$, $Cl^-(aq)$ and $H_2O(l)$
	Electrodes	Inert electrodes e.g. graphite
	Cathode (–)	$2H_2O + 2e \rightleftharpoons H_2 + 2OH^-$ $E^\ominus = -0.83$ V $Na^+ + e \rightleftharpoons Na$ $E^\ominus = -2.71$ V Since the $E^\ominus(H_2O/H_2)$ is less negative than $E^\ominus(Na^+/Na)$, **H_2O has a greater tendency to be reduced than Na^+** and is thus *preferentially* discharged. ∴ At the cathode, $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
	Anode (+)	$O_2 + 4H^+ + 4e \rightleftharpoons 2H_2O$ $E^\ominus = +1.23$ V $Cl_2 + 2e \rightleftharpoons 2Cl^-$ $E^\ominus = +1.36$ V Since the $E^\ominus(O_2/H_2O)$ is less positive than $E^\ominus(Cl_2/Cl^-)$, **H_2O has a greater tendency to be oxidised than Cl^-** and is thus *preferentially* discharged. ∴ At the anode, $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
	Overall equation	$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$ The electrolysis of NaC*l*(aq) results in the **electrolysis of water!**

Note:

- For the half-equations and overall redox equation, use '→' instead of '⇌'.
- $[H^+]$ and $[OH^-]$ from the auto-ionisation of water are extremely low at 10^{-7} mol dm^{-3} so their discharge is not significant.

In summary,

- cations are Discharged at the cathode. If more than one cation is present, and the *concentration of the cations are almost the same*, the cation with a More positive/less negative $E^\ominus$ will generally be reduced. [The reduction of H_2O, if present, must also be considered.]

- anions are Discharged at the anode. If more than one anion is present, and the *concentration of the anions are almost the same*, the anion with a More negative/less positive $E^\ominus$ will generally be oxidised. [The oxidation of H_2O, if present, must also be considered.]

(C) Relative Concentrations of the Species (especially when $E^⦵$ values are close)

The $E^⦵$ value used to predict the species to be discharged is valid under *standard conditions*. However, if the concentrations of the species are **non-standard,** i.e. not 1.0 mol dm^{-3}, then we need to consider its effect on the position of equilibrium and hence the value of E, the electrode potential under non-standard conditions.

For example, the presence of high concentrations of an ion may cause it to be discharged even though its $E^⦵$ value predicts it to be less favourable (at standard conditions).

Consider the electrolysis of brine (*concentrated* sodium chloride, where concentrations of Na^+ and Cl^- are very high).

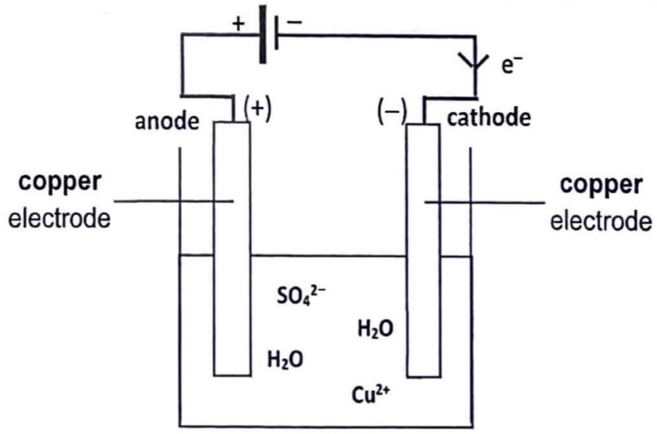
Brine (conc. aqueous NaCl)	**Species present in electrolyte**	$Na^+(aq)$, $Cl^-(aq)$ and $H_2O(l)$
	Electrodes	Inert electrodes e.g. graphite
	Cathode (–)	$Na^+(aq) + e^- \rightleftharpoons Na(s)$ $E^⦵ = -2.71$ V $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$ $E^⦵ = -0.83$ V The higher $[Na^+]$ **does not** override the position of the ions in the redox series as its reduction potential is **too** negative.
	Anode (+)	$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ **Reasons:** $O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$ $E^⦵ = +1.23$ V $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E^⦵ = +1.36$ V • The increased $[Cl^-]$ causes the position of equilibrium of $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ to shift left, such that E becomes much less than +1.36 V (i.e. and also less positive than $E^⦵(O_2/H_2O)$. • **$Cl^-(aq)$ is preferentially discharged to form $Cl_2(g)$.**

(D) Nature of the Electrodes (Inert vs Reactive)

An inert electrode, such as the graphite or platinum electrode, does not participate in the electrolysis reactions.

A reactive electrode is one that participates in the electrolysis reactions. Since it participates in the electrolysis reactions, the reactive electrode (the anode, in particular) must be considered in addition to species present in the electrolyte.

Consider the electrolysis of $CuSO_4(aq)$ using **reactive** copper electrodes.

$CuSO_4(aq)$	**Species present in electrolyte**	$Cu^{2+}(aq)$, $SO_4^{2-}(aq)$ and $H_2O(l)$
	Electrodes	Cu electrodes (reactive electrodes)
	Cathode (–)	Cu^{2+} and H_2O compete to undergo reduction. $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $E^\ominus = +0.34$ V $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$ $E^\ominus = -0.83$ V Since $E^\ominus(Cu^{2+}/Cu)$ is positive, **Cu^{2+} has a greater tendency to be reduced than H_2O** and is thus *preferentially* discharged. **Reaction at cathode:** $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ [Note: The sulfate ions will be repelled by the negative cathode. Hence, they will not be reduced.]
	Anode (+)	SO_4^{2-}, H_2O and **Cu (from the electrode)** compete to undergo oxidation. $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $E^\ominus = +0.34$ V $O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$ $E^\ominus = +1.23$ V $S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$ $E^\ominus = +2.01$ V Since $E^\ominus(Cu^{2+}/Cu)$ is the least positive, **Cu has the greatest tendency to be oxidised** and is thus *preferentially* discharged. Thus the anode reaction is: **Reaction at anode:** $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
	Setup	

What if **INERT** electrodes such as graphite were used instead?

Cathode **(–)**	Cu^{2+} and H_2O compete to undergo reduction. Since the considerations are the same, Cu^{2+} is still preferentially discharged. **Reaction at cathode:** $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
Anode **(+)**	SO_4^{2-}, H_2O ~~and Cu (from the electrode)~~ **(inert electrode, so no need to consider Cu)** compete to undergo oxidation. $O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$ $E^\ominus = +1.23$ V $S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$ $E^\ominus = +2.01$ V We do not need to consider the Cu^{2+}/Cu equation. Here, since $E^\ominus(O_2/H_2O)$ is less positive, **H_2O has a greater tendency to be oxidised** and is thus preferentially discharged. **Reaction at anode:** $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Summary of examples illustrated from pages 4 to 8

	(a) molten sodium chloride using **graphite electrodes**	**(b) aqueous sodium chloride** using **graphite electrodes**	**(c) aqueous copper(II) sulfate** using **copper electrodes**
Electrolyte	$NaCl(l)$	$NaCl(aq)$	$CuSO_4(aq)$
Ions present	$Na^+(l)$, $Cl^-(l)$	$Na^+(aq)$, $Cl^-(aq)$	$Cu^{2+}(aq)$, $SO_4^{2-}(aq)$
Other species	–	$H_2O(l)$	$H_2O(l)$
Electrodes	C (i.e. inert)	C (i.e. inert)	Cu (i.e. anode is **reactive**)
At cathode	**$Na^+(l) + e^- \rightarrow Na(l)$**	$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$, $E^\ominus = -0.83$ V $Na^+\text{-}(aq) + e^- \rightleftharpoons Na\text{-}(s)$, $E^\ominus = -2.71$ V **$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$**	$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$, $E^\ominus = +0.34$ V $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$, $E^\ominus = -0.83$ V **$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$**
At anode	**$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$**	$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$, $E^\ominus = +1.23$ V $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$, $E^\ominus = +1.36$ V **$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$**	$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$, $E^\ominus = +0.34$ V $O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$, $E^\ominus = +1.23$ V $2S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$ $E^\ominus = +2.01$ V **$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$**
Overall reaction	$2Na^+(l) + 2Cl^-(l) \rightarrow 2Na(l) + Cl_2(g)$	$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$	NA
Observation	A shiny metallic liquid is formed at the cathode and a greenish–yellow gas is liberated at the anode.	A colourless gas evolves at each electrode. Volume ratio of H_2: O_2 = 2:1	Copper cathode increases in size and copper anode decreases in size. There is no change in the colour of the copper(II) sulfate solution.
Remarks	In general, for the electrolysis of a molten ionic compound, the metal ion is discharged as $M(l)$ or $M(s)$ at the cathode and the non–metal anion is discharged at the anode e.g. as $X_2(g)$ (when X = H, O, N, F, Cl, Br, I).	Often, the electrolysis of a dilute, aqueous solution of an ionic salt is in fact the electrolysis of water. The concentrations of H^+ and OH^- from the auto-ionisation of water are far too low (10^{-7} mol dm^{-3}). Hence we do not consider them here. If the **$[Cl^-(aq)]$ is high** e.g. concentrated $NaCl$, then the product at the anode is Cl_2: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$	Metals with reactivity above Pt (Mg, Zn, Fe, Pb, Cu, Ag, Au) are reactive electrodes and dissolve during electrolysis. Even though Al is a reactive metal, it is protected by a dense oxide layer so that the Al electrode is inert. Hence an Al anode is not oxidised during electrolysis. Instead, the anions in solution are oxidised. (Refer to section C1 on anodising of aluminium)

3 INDUSTRIAL APPLICATIONS OF ELECTROLYSIS

Candidates should be able to 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]

3.1 Anodising of Aluminium

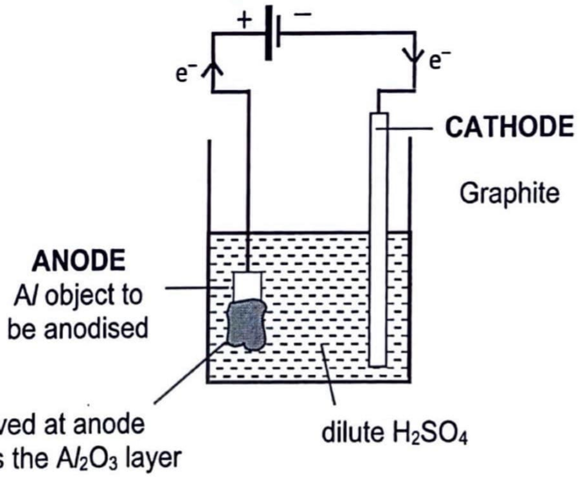
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$ $E^\ominus = -1.66$ V
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$ $E^\ominus = +1.23$ V

Based on the very negative $E^\ominus$ value, Al should be highly reactive (i.e. higher tendency to be oxidised than water and hence preferentially discharged at the anode in an electrolytic cell).

However, in reality, aluminium is not oxidised during electrolysis and is highly corrosion resistant. Why is this so?

Reason: Aluminium when exposed to oxygen in the air acquires a protective layer of **aluminium oxide** which protects the underlying metal from water and any further chemical attack.

Although this protective layer forms naturally from air, the layer is not thick enough and can be enhanced through anodising. The process of coating aluminium objects with aluminium oxide via electrolysis is called **anodising.**



Electrolyte: dilute sulfuric acid or chromic(VI) acid

Anode: **Aluminium object** to be anodised

$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ +2.01 V
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ +1.23 V
Since H_2O is preferentially oxidised,
$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Oxygen evolved at the anode reacts with the aluminium and the surface oxide layer of Al_2O_3 is thickened.

$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$

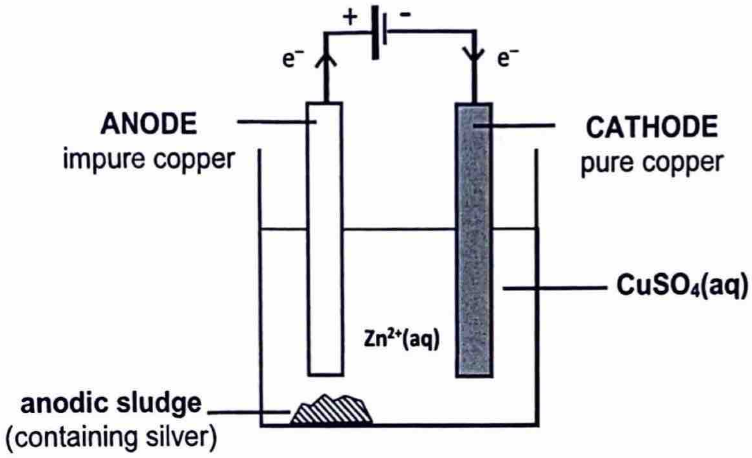
Advantages of anodising:

- Anodising of aluminium is of substantial commercial value as aluminium is widely used especially where lightness and corrosion resistance are important e.g. cookware, electric cables, aircrafts and automobile.
- The anodic film is hard, resistant to wear and a good electrical insulator.
- The freshly formed film can be dyed to give colour–anodised aluminium.

3.2 Electrolytic Purification of Copper

Copper is about 99% pure when it is first obtained from its ores. The main impurities are silver, platinum, iron, gold and zinc.

The impurities reduce the electrical conductivity of copper and so impure copper must be purified before being used e.g. for electrical wires. The purification of metals is known as *refining*.



Electrolyte: $CuSO_4(aq)$

Cathode: Pure copper

Anode: Impure copper to be refined.

At the cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

At the anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

The cell potential is adjusted such that Cu at the anode dissolves. Over a period of time the **anode dissolves** and **reddish-brown copper is deposited on the cathode.**

Impurities with $E^\ominus$ values more positive than Cu e.g. Ag

$Ag^+ + e^- \rightleftharpoons Ag$ $\quad E^\ominus = +0.80$ V
$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $\quad E^\ominus = +0.34$ V

Since the $E^\ominus(Cu^{2+}/Cu)$ is less positive, Cu is preferentially oxidised at the anode. Thus Ag impurities will not be oxidised and they fall to the bottom as 'sludge'.

Impurities with $E^\ominus$ values less positive than Cu e.g. Zn

$Zn^{2+} + 2e^- \rightleftharpoons Zn$ $\quad E^\ominus = -0.76$ V
$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $\quad E^\ominus = +0.34$ V

Since the $E^\ominus(Zn^{2+}/Zn)$ is less positive, Zn is preferentially oxidised at the anode and goes into the solution (as Zn^{2+} ions) first, followed by Cu.

At the cathode, however, since the $E^\ominus(Cu^{2+}/Cu)$ is more positive, Cu^{2+} is preferentially reduced and deposited on the pure Cu rod. Zn^{2+} ions remain in the electrolyte and are not plated onto the cathode.

3.3 Electroplating

Cathode: object to be plated
Anode: plating metal
Electrolyte: a solution containing the ions of the plating metal

Only metals less reactive than zinc (e.g. $E^\ominus$ more positive than that of Zn) can be used as plating metal. Hence, objects may be electroplated with chromium, copper, silver and gold but cannot be electroplated with aluminium for example.

Successful electroplating requires that the electric current, concentration of electrolyte and temperature to be exactly right. The cathode must also be clean.

4 FARADAY'S LAW OF ELECTROLYSIS

Candidates should be able to state the relationship, $F = Le$, between the Faraday constant, the Avogadro constant and the charge on the electron.

Faraday's laws of electrolysis provide the quantitative relationship between electricity and chemical change.

4.1 Faraday's First Law

The mass of substance and/or volume of gas liberated during electrolysis is **directly proportional** to the **amount of charge** that passed through the cell.

$$m \propto Q \text{ where } \underline{Q = It}$$

Q = amount of charge in coulombs, **C**
I = current in amperes, **A**
t = time in seconds, **s**
m = mass deposited in grams, **g**

When a current of 1 A has been passed for 1 s, this means that 1 C of charge has been passed.

Important: The amount of substance formed is **not** dependent on the temperature or concentration.

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

The greater quantity of electricity, **Q**, passed through the cell
⇒ a greater amount of e^- passed through
⇒ a greater mass of Cu(s) deposited.

This can be achieved by using a higher current or passing the current through for a longer duration. Increasing the concentration of Cu^{2+} will **not** result in a greater mass of Cu(s) deposited within the same duration.

The Faraday's constant

One Faraday, **F** (in C mol^{-1}), is the charge carried by 1 mole of electrons.

F = *L* e

L = Avogadro Constant = 6.02×10^{23} mol^{-1}
e = charge on one electron = -1.60×10^{-19} C
1 F = $6.02 \times 10^{23} \times 1.60 \times 10^{-19}$
= **96500 C mol^{-1}**

Since 1 mol of e$^-$ carries 96500 C, we can relate the amount of e$^-$ passed through the circuit with the total quantity of charge, **Q**, passed through, per mole of reaction i.e.

$$\text{Amount of electrons, } n_e = \frac{Q}{96500} \text{ mol} \quad \Rightarrow \quad \mathbf{Q = n_eF}$$

Where n$_e$ = no. of mol. of electron per mol. of reaction

4.2 Faraday's Second Law

Candidates should be able to calculate:
(i) the quantity of charge passed during electrolysis
(ii) the mass and/or volume of substance liberated during electrolysis

The amount of charge required to discharge 1 mole of an element depends on the **charge on the ion**.

In other words, the **number of Faradays** required to discharge one mole of an ion at the electrode **equals the number of charges** on the ion.

To discharge	Implications
1 mol of Na^+ requires 1 F (or 96500 C) of electrons	$Na^+ + e^- \rightarrow Na$ 96500 C is needed to produce 23.0 g of Na
1 mol Mg^{2+} requires 2 F (or 2 x 96500 C) of electrons	$Mg^{2+} + 2e^- \rightarrow Mg$ It requires 193 000 C to produce 24.3 g of Mg
1 mol Al^{3+} requires 3 F (or 3 x 96500 C) of electrons	$Al^{3+} + 3e^- \rightarrow Al$ It requires 289 500 C to produce 27.0 g of *Al*

Worked Example 1:

What is the mass of Cu deposited on the cathode of an electrolytic cell if an electric current of 2.00 A is run through $CuSO_4(aq)$ for 20.0 minutes?

Answer:	**Answer:**
Quantity of charge passed = I x t = 2.00 x 20.0 x 60 = 2400 C $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ 2 x 96500 C is required to deposit 1 mol of Cu Amt of Cu(s) deposited = 2400 ÷ (2 x 96500) = 0.01244 mol Mass of Cu(s) deposited = 0.01244 x 63.5 = <u>**0.790 g**</u>	Since Q = It = n$_e$F $n_e = \frac{It}{F} = \frac{(2.00)(20\times60)}{96500} = 0.02487$ mol $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ Amt of Cu deposited = ½(0.02487) = 0.01244 mol Mass of Cu(s) deposited = 0.01244 x 63.5 = <u>**0.790 g**</u>

Worked Example 2:

What is the time needed to deposit 1.00 g chromium when a current of 0.120 A flows through $Cr_2(SO_4)_3(aq)$?

Answer:
Amount of Cr deposited = 1.00 ÷ 52.0
= 0.01923 mol

$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$
3 x 96500 C is required to deposit 1 mol of Cr

Quantity of charge needed to deposit 0.01923 mol
= 0.01923 (3 x 96500) = 5567.3 C

Time needed = Q / I = 5567.3 ÷ 0.120
= 46394.2 s ≈ **12.9 h**

Answer:
Amount of Cr deposited = 1.00 ÷ 52.0
= 0.01923 mol

$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$

$n_e = 3(0.01923) = 0.05769$ mol

Since $Q = It = n_eF$

$$t = \frac{n_eF}{I} = \frac{(0.05769)(96500)}{0.120}$$
$$= 46392.4 \text{ s} \approx 12.9 \text{ h}$$

Worked Example 3:

Calculate the volume of oxygen (at s.t.p) produced when 2 A current is passed through dilute sulfuric acid for a period of 30 min using Pt electrodes.

Answer:
Quantity of charge passed
= I x t = 2 x 30 x 60 = 3600 C

Anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
4 x 96500 C is required to produce 1 mol of O_2

Amount of O_2 produced = 3600 ÷ (4 x 96500)
= 9.326×10^{-3} mol

Volume of O_2 produced = 9.326×10^{-3} x 22.7
= **0.212 dm^3**

Answer:
Anode: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

$$n_e = \frac{It}{F} = \frac{(2)(30 \times 60)}{96500} = 0.03731 \text{ mol}$$

Amt of O_2 produced = $(^1/_4)(0.03731)$
= 9.326×10^{-3} mol

Volume of O_2 produced = 9.326×10^{-3} x 22.7
= **0.212 dm^3**

Worked Example 4:

A current is passed through 2 cells connected in series. The 1st cell contains $XSO_4(aq)$ while the 2nd cell contains $Y_2SO_4(aq)$. The relative atomic masses of X and Y are in the ratio of 1:3. What is the ratio of the mass of X liberated to that of Y?

Answer:
Let m_X be mass of X liberated and M_X be molar mass of X;
Let m_Y be mass of Y liberated and M_Y be molar mass of Y.

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

For the **same quantity of electricity**, amt of X liberated = ½ x amt of Y
$n_X = \frac{1}{2} n_Y$

Therefore,

$$\frac{m_X}{M_X} = \frac{1}{2} \times \frac{m_Y}{M_Y}$$

$$\frac{m_X}{m_Y} = \frac{1}{2} \times \frac{M_X}{M_Y}$$

Since $M_Y = 3 \times M_X$ $\frac{m_X}{m_Y} = \frac{1}{2} \times \frac{1}{3} = \frac{1}{6}$

The ratio of mass of X:Y = **1:6**

RAFFLES INSTITUTION
YEAR 6 H2 CHEMISTRY 2023
Tutorial 21b: Electrochemistry 2

Self-Check

1 Predict, with reasons, the products formed at the anode and at the cathode, when aqueous nickel(II) bromide is electrolysed using nickel electrodes. Describe what will be observed at each electrode.

2 **(a)** An aluminium object with a surface area of 500 cm^2 is to be anodised. How many coulombs of electricity are needed to increase the oxide layer by 1×10^{-3} cm in thickness? (Density of Al_2O_3 = 4.0 g cm^{-3})

(b) Calculate the ratio of the mass of silver to the mass of nickel deposited on the cathodes when an electrolytic cell containing aqueous silver nitrate and aqueous nickel(II) sulfate connected in series.

(c) When a current is passed through a cell containing $CuSO_4$(aq) using inert electrodes, copper is deposited at the cathode while oxygen is evolved at the anode. What volume of oxygen at standard temperature and pressure would be produced if enough current were passed for a sufficient time to deposit 0.635 g of copper?

3 A 1 mol dm^{-3} aqueous copper(II) salt is electrolysed between copper electrodes, using a constant current for 60 s.

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only Is correct

What affects the mass of copper deposited on the cathode?

1 decreasing the time taken
2 increasing the concentration of the solution
3 the nature of the anion present

N2012/I/32

4 Two separate electrolyses were performed as follows, under the same conditions of temperature and pressure.

1 When molten copper(II) chloride was electrolysed for five minutes, 100 cm^3 of chlorine were collected from the anode.
2 When aqueous sulfuric acid was electrolysed for five minutes, 200 cm^3 of oxygen were collected from the anode.

If the current used in electrolysis 1 was I, what was the current used in electrolysis 2?

A $0.5I$ **B** I **C** $2I$ **D** $4I$

N2012/I/7

5 In the electrolysis of molten aluminium oxide, 0.27 g 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}

N2021/I/27

Discussion Questions

6 Using inert electrodes, a current was passed through two beakers containing aqueous silver nitrate and aqueous chromium(III) sulfate respectively and connected in series.

After 30 min, 0.100 g of silver was deposited from the first solution.

Calculate

(a) the number of moles of silver deposited;

(b) the current passed;

(c) the mass of chromium deposited from aqueous chromium(III) sulfate.

7 Explain the following as fully as you can. Quote relevant $E^\ominus$ when appropriate.

(a) Lead is extracted by reduction of its oxide with carbon, whereas aluminium has to be extracted by electrolysis of its molten ore.

(b) Chlorine is commercially made by the electrolysis of concentrated aqueous sodium chloride (brine). However, fluorine cannot be produced using the same method like chlorine.

Modified from 2012 RI PrelimP2Q3(a)

8 **(a)** 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 the purification procedure.

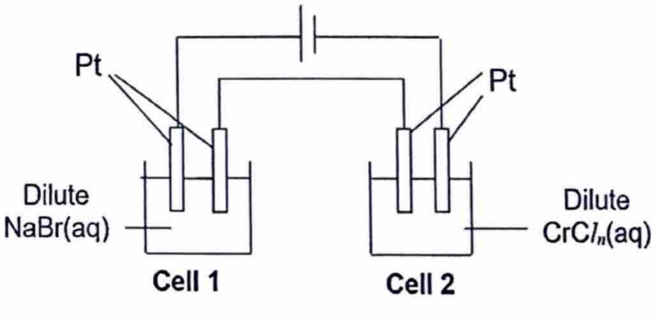
(b) A current of 2.00 A was passed through the cell in **(a)** for 23.0 min, and the electrodes removed, washed, dried and weighed. It was found that the anode had lost 0.950 g. After filtering it off and drying it, the deposit underneath the anode weighed 0.0500 g. On adding an excess of dimethyloxime to the electrolyte, the highly insoluble red complex with the formula of $Ni(C_4H_7N_2O_2)_2$ 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 and silver removed from the alloy.

2014/3/5(d) and (e)

9 *Use of the Data Booklet is relevant to this question.*
The figure below shows two cells connected in series. **Cell 1** and **Cell 2** involve the electrolysis of a dilute solution of NaBr and $CrCl_n$ respectively.



(a) Write ionic equations for the reactions occurring at the cathode and anode in **Cell 1** during electrolysis.

(b) A current was passed through the dilute solution of NaBr in **Cell 1** for 10 minutes. The product formed at the anode required 35.60 cm^3 of 0.500 mol dm^{-3} of thiosulfate ions, $S_2O_3^{2-}$, for complete reaction, giving SO_4^{2-} as the sulfur-containing product.

Write a balanced ionic equation for the reaction between the anode product and sodium thiosulfate. Hence, calculate the number of moles of electrons that passed through the circuit.

(c) In the same 10 minutes, 3.68 g of chromium was deposited at one of the electrodes in **Cell 2**. Calculate the value of n in $CrCl_n$.

2018 RI CT2 Section C 1d

10 The cathode of a cell is a square piece of copper with dimensions 0.1 m x 0.1 m. The electrolyte is copper(II) sulfate.

Assume that each copper atom occupies a cube of length 3.0×10^{-12} m, the piece of copper has no thickness and that there is a uniform coverage.

The Faraday constant = 9.65×10^4 C $mo1^{-1}$.

How long will it take a current of 4.0 A to cover both sides of the piece of copper with new copper to a total depth of 2000 atoms (1000 atoms on each side)?

2019/1/30