Electrochemistry

Part Two: The Electrolysis of Aqueous Salts, Acids and Alkalis



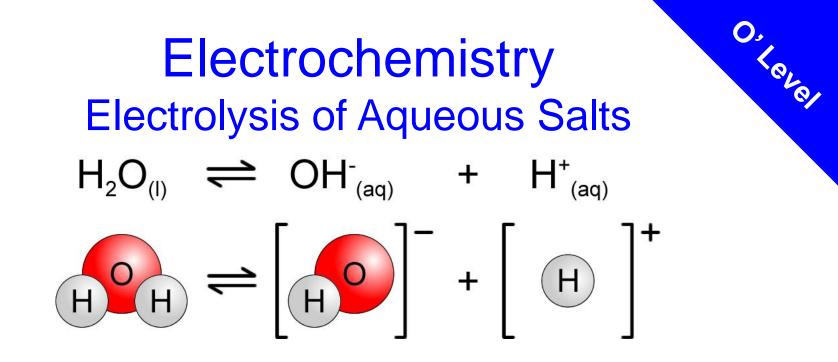
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What happens during the electrolysis of an aqueous salt using inert electrodes?



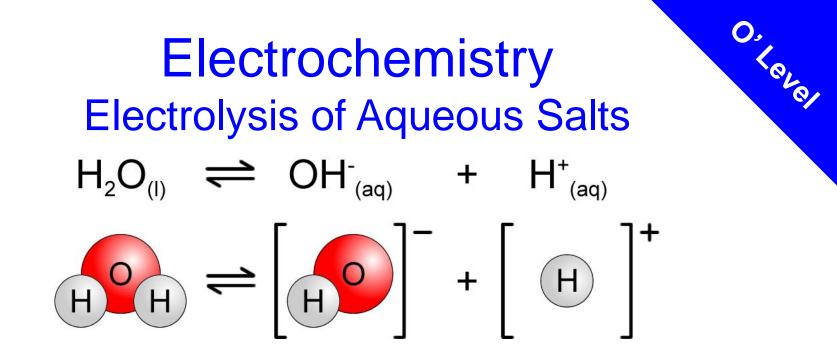
- Remember, not all ionic compounds are soluble in water! For example...
 - \rightarrow Barium sulfate, BaSO₄ insoluble!
- \rightarrow Calcium carbonate, CaCO₃ insoluble!
 - → Copper(II) oxide, CuO insoluble!
 - \rightarrow Lead(II) iodide, PbI₂ insoluble!
 - \rightarrow Silver chloride, AgCl insoluble!





- Water molecules spontaneously dissociate (ionize) to form *hydroxide ions* and *hydrogen ions*:
- The concentrations of the hydroxide ions and hydrogen ions are relatively low (1 × 10⁻⁷ mol/dm) but their presence in solution still affects the products that are formed during the electrolysis of *aqueous salts*.

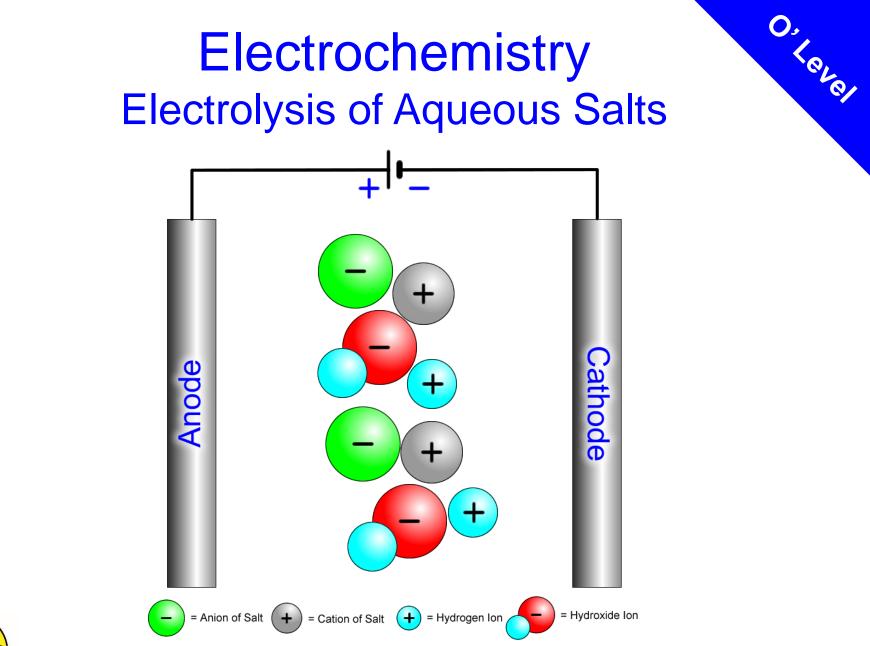




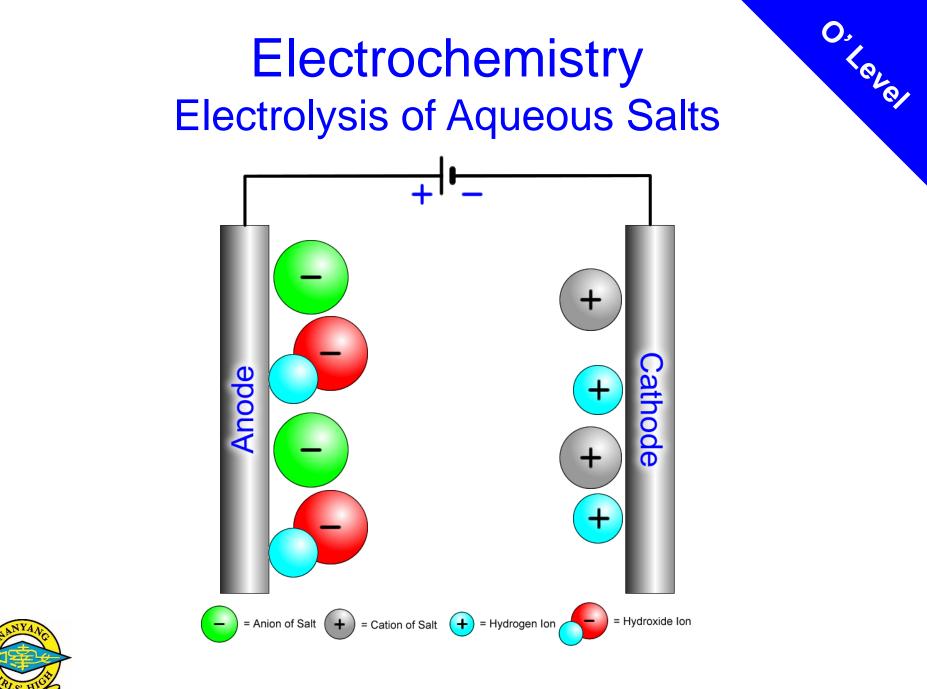
 During the electrolysis of an aqueous salt solution, hydroxide ions, as well as anions from the salt itself, will be attracted to the anode.

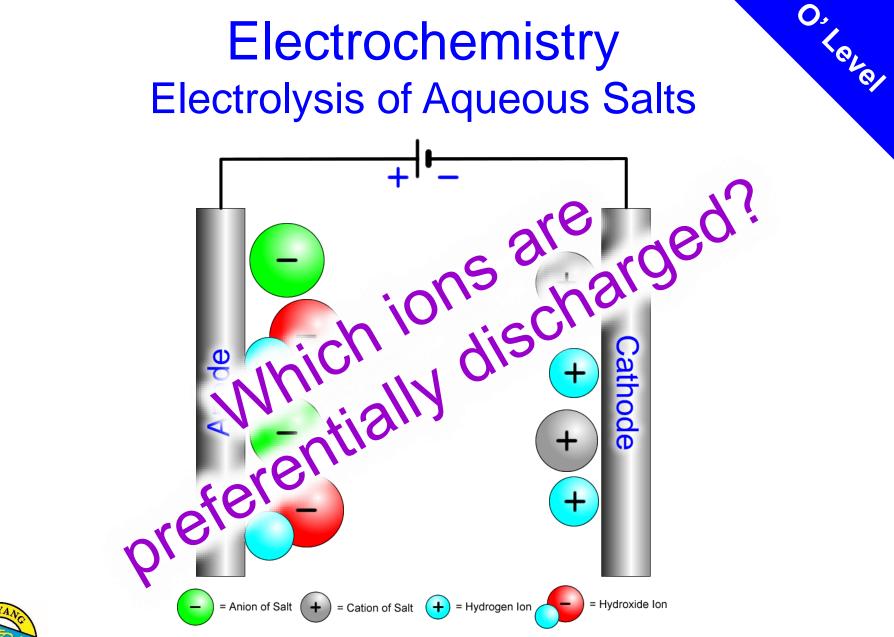
• During the electrolysis of an aqueous salt solution, hydrogen ions, as well as cations from the salt itself, will be attracted to the *cathode*.













 If the aqueous salt solution is *dilute*, hydroxide ions are oxidised at the anode and effervescence is observed as oxygen gas is produced:

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

(Hydroxide ions are oxidised to form molecular oxygen)

 If the aqueous salt solution is *concentrated*, the anion of the salt is oxidised at the anode.

• Note: Regardless of concentration, *carbonate ions*, *nitrate ions* and *sulfate ions* are *not* oxidised during the electrolysis of aqueous salt solutions.



 If the cation of the salt is *above hydrogen* in the electrochemical series, then hydrogen ions are reduced at the cathode and effervescence is observed as hydrogen gas is produced:

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

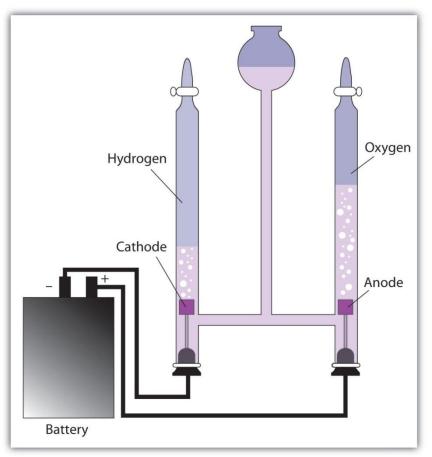
(Hydrogen ions are reduced to form molecular hydrogen)

• If the cation of the salt is *below hydrogen* in the electrochemical series, then the cation of the salt is reduced at the cathode.



Electrolysis of Water

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• Anode: $4OH^{-}(aq) \rightarrow O_{2}(g) + 2H_{2}O(l) + 4e^{-}$ • Cathode: $2H^{+}(aq) + 2e^{-}H_{2}(g)$

- Potassium K⁺
 - Sodium Na⁺
- Calcium Ca²⁺
- Magnesium Mg²⁺
 - Aluminium Al³⁺
 - Zinc Zn²⁺
 - Iron Fe^{2+ / 3+}
 - Lead Pb²⁺
 - Hydrogen H⁺
 - Copper Cu²⁺
 - Silver Ag⁺

During electrolysis of the aqueous salt, *e.g.* CaCl₂, hydrogen gas is produced at the cathode, <u>not</u> the metallic element.
2H⁺(aq) + 2e⁻ → H₂(g)

• These metals can only be extracted from their compounds by electrolysis of the molten salt, <u>not</u> electrolysis of the aqueous salt.

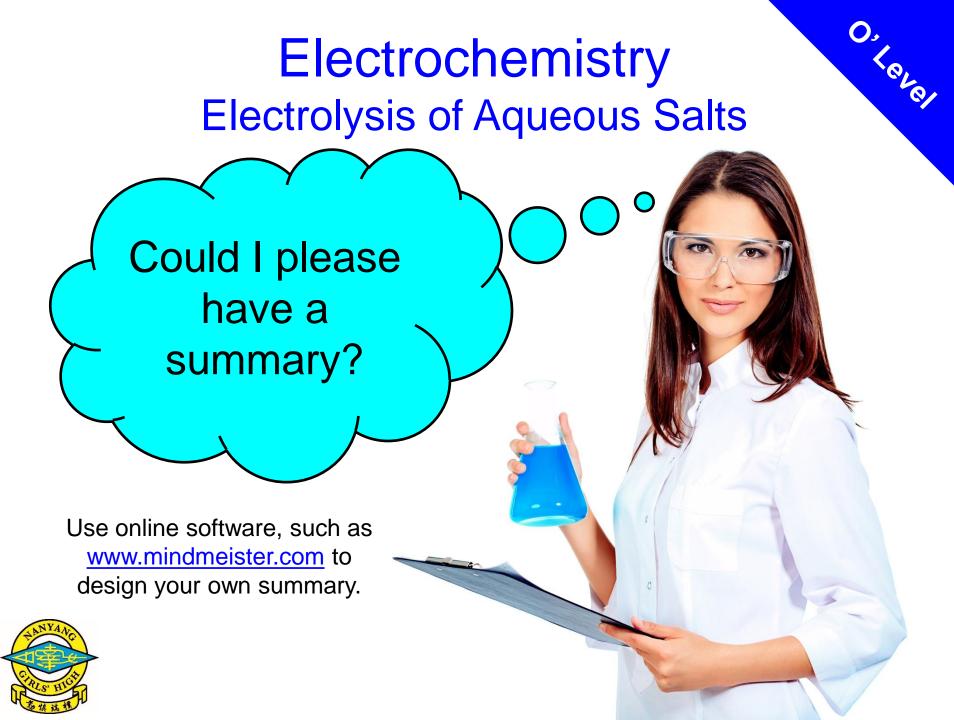
• During electrolysis of the aqueous salt, *e.g.* CuCl₂, the metallic element is produced at the cathode, <u>not</u> hydrogen gas.

- Sulfate SO₄^{2–}
 - Nitrate NO_3^-
 - Chloride C*l*-
 - Bromide Br-
 - lodide I[–]
- Hydroxide OH-

• Not oxidised during electrolysis of the aqueous salt.

- Oxidised <u>only</u> if the aqueous solution is <u>concentrated</u>, *e.g.* a concentrated solution of sodium bromide.
- The hydroxide ion is readily oxidised at the anode.
 4OH⁻(aq) → 2H₂O(l) + O₂(g) + 4e⁻





- Electrolysis of a molten binary salt, e.g. MX, where M is a metallic element and X is a non-metallic element:
- → lons of metal M are *reduced* at the *cathode* to produce the metallic element. $M^{n+}(l) + ne^{-} \rightarrow M(l)$

→ lons of non-metal X are *oxidised* at the *anode* to produce the non-metallic element. $2X^{n-}(l) \rightarrow X_2(l) + 2ne^{-}$



• Electrolysis of an *aqueous salt*:

→ If the metal is *above hydrogen* in the electrochemical series, then *hydrogen ions* are preferentially reduced at the cathode to produce hydrogen gas: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

→ If the metal is *below hydrogen* in the electrochemical series, then *metal ions* are preferentially reduced at the cathode to produce the metallic element: $M^{n+}(aq) + ne^{-} \rightarrow M(s)$



• Electrolysis of an aqueous salt.

→ If the aqueous solution is *dilute*, or it contains the *salt* of a nitrate or sulfate, then hydroxide ions are preferentially oxidised at the anode to produce oxygen gas and water:

 $4OH^{-}(aq) \rightarrow O_{2}(g) + 2H_{2}O(l) + 4e^{-}$

→ If the aqueous solution is a concentrated solution of either a chloride, bromide or iodide, then the chloride, bromide or iodide ions are preferentially oxidised at the anode to produce the Group 17 element:

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



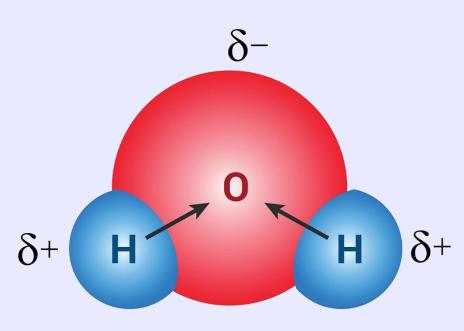
• Aqueous electrolytes are aqueous solutions of ionic compounds or acids (*i.e.* solutions that contain mobile cations, anions and water molecules).

 Because aqueous electrolytes contain cations, anions and water molecules, rules need to be established to determine what will be *selectively discharged* at the electrodes.

→ What will be selectively *oxidised* at the *anode*, *anions* or *water molecules*?

→ What will be selectively reduced at the cathode, cations or water molecules?





• A polar water molecule.

 Due to an uneven distribution of electrons within a molecule of water, the oxygen atom
carries a *slight negative charge* (δ–) while the two hydrogen atoms each carry a *slight positive charge* (δ+).

 Consequently, water molecules are attracted towards the anode and the cathode during the electrolysis of aqueous electrolytes.



 During the electrolysis of aqueous electrolytes, only one species can be oxidised at the anode, and only one species can be reduced at the cathode.

• When there is more than one species competing to be discharged at the same electrode, the one that requires the *least energy* to be discharged will be *selectively discharged*.

 The order in which chemical species are selectively discharged is determined by their *standard electrode potentials* (symbol *E*[⊕]). Based upon their standard electrode potentials, chemical species are arranged in an *electrochemical series*.



- ***** Factors Affecting Selective Discharge:
- (a) Position in the electrochemical series.

• An *electrochemical series* is a series in which species are arranged in an increasing or decreasing order of their standard electrode potential, E^{\ominus} values.

 The electrode (reduction) potential (E) is a value which shows how easily a species is reduced. By convention, the half-reactions are written as *reductions* (*i.e.* the electrons are written on the left-hand-side). This means that in these reversible half-equations, the *forward reactions* (→) demonstrate *reduction* while the *backward reactions* (←) demonstrate *oxidation*.



The more positive (or less negative) an electrode potential, the more likely it is for that species to undergo reduction.

The more positive (or less negative) an electrode potential, the more likely it is for that species to be selectively reduced at the cathode.

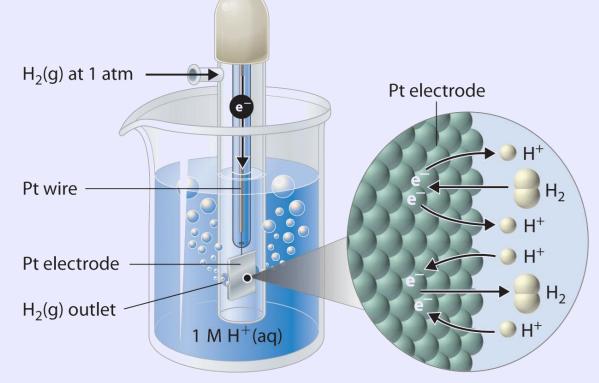


Electrochemistry

Electrochemistry				
At the Cathode	Half-equations	<i>E</i> ⊖ / V	Ease of Discharge	
K+	$K^+ + e^- \rightleftharpoons K$	- 2.92		
Na+	Na⁺ + e⁻ ≓ Na	- 2.71		
Mg ²⁺	$Mg^{2+} + 2e^- \rightleftharpoons Mg$	- 2.36	hich d.	
A <i>l</i> ³⁺	$Al^{3+} + 3e^- \rightleftharpoons Al$	- 1.68	th w duce	
H ₂ O	$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	-0.83	e wi	
Zn ²⁺	Zn ²⁺ + 2e⁻ ≓ Zn	-0.76	eas are	
Fe ²⁺	Fe ²⁺ + 2e ⁻ ≓ Fe	-0.44	tions	
Pb ²⁺	$Pb^{2+} + 2e^- \rightleftharpoons Pb$	- 0.13	Increasing ease with which the cations are reduced.	
H+	$2H^+ + 2e^- \Rightarrow H_2$	0.00	the	
Cu ²⁺	$Cu^{2+} + 2e^{-} \rightleftharpoons Cu$	+0.34	•	
Ag+	$Ag^+ + e^- \rightleftharpoons Ag$	+0.80		



 Standard electrode potentials are measured relative to the Standard Hydrogen Electrode (SHE).

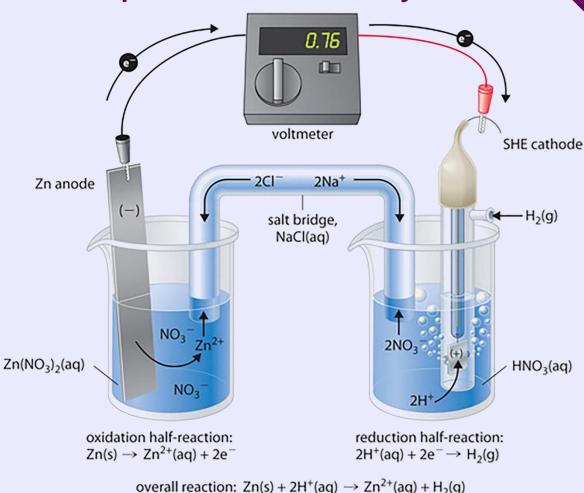


half-reaction at Pt surface: $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$

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 Measuring the standard electrode potential of the zinc half-cell relative to the Standard
Hydrogen Electrode.



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Electrochemistry Electrolysis of Aqueous Electrolytes At the cathode, reduction of the cations with the more positive (or less negative) E^{\ominus} will take place.

Example 1: the *positive* standard electrode potential of silver (*E*[⊖] = +0.80 V) suggests that *it is likely* that the silver ions (Ag⁺) will be *reduced* to form silver atoms (Ag) at the cathode.

Ag⁺ + e⁻
$$\rightleftharpoons$$
 Ag E^{\ominus} = +0.80 V
Ag⁺ + e⁻ → Ag
likely to happen



Electrochemistry Electrolysis of Aqueous Electrolytes At the cathode, reduction of the cations with the more positive (or less negative) E^{\ominus} will take place.

Example 2: The negative standard electrode potential of sodium (E[⊕] = -2.71 V) suggests that *it is unlikely* that the sodium ions (Na⁺) will be reduced to form sodium atoms (Na) at the cathode.

Na⁺ + e⁻ \rightleftharpoons Na $E^{\ominus} = -2.71$ V Na⁺ + e⁻ → Na *unlikely to happen*



At the cathode, reduction of the cations with the more positive (or less negative) E^{\ominus} will take place.

• Example 3: The chemical species present in the electrolyte are Na⁺ and H_2O .

Na⁺ + e⁻ \rightleftharpoons Na $E^{\ominus} = -2.71$ V

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

Since H₂O is lower in the electrochemical series than Na⁺ (*i.e.* $E^{\ominus}(H_2O|H_2)$) is more positive or less negative than $E^{\ominus}(Na^+|Na)$), H₂O has a higher tendency to be reduced than Na⁺, so H₂O is preferentially reduced at the cathode, resulting in effervescence of hydrogen gas.



 $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Electrochemistry

- V 5 DOARED FOR Selective discharge of anions can be deduced from the following section of the electrochemical series.
- At the *anode*, *oxidation* of the *anions* with the *less positive* (or more negative) E^{\ominus} takes place.

At the Anode	Half-equations	Е[⊖] / V	Ease of Discharge
F-	$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87	which sed.
SO ₄ ²⁻	$S_2O_8^{2-} + 2e^- \Rightarrow 2SO_4^{2-}$	+2.01	
C <i>l</i> −	Cl_2 + $2e^- \rightleftharpoons 2Cl^-$	+1.36	e with oxidis
H ₂ O	$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23	l ease s are o
Br−	$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07	easing anions
I-	$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54	Increa the a
OH-	$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	+0.40	



- At the anode, oxidation of the anions with the less positive (or more negative) E^{\ominus} will take place.
- Example 4: The very small positive standard electrode potential of OH⁻ suggests that it is likely that the hydroxide ions (OH⁻) will be oxidised to form H₂O and O₂ at the anode.
- The half-equation for E^{\ominus} is always written as *reduction*: $O_2 + H_2O + 4e^- \rightleftharpoons 4OH^- E^{\ominus} = +0.40 V$

The reverse reaction must be written to show oxidation: $4OH^- \rightarrow O_2 + H_2O + 4e^$ *likely to happen*



- At the anode, oxidation of the anions with the less positive (or more negative) E^{\ominus} will take place.
- Example 5: The very large positive standard electrode potential of F⁻ suggests that *it is unlikely* that the fluoride ions (F⁻) will be *oxidised* to form F₂ at the anode.
- The half-equation for E^{\ominus} is always written as *reduction*: $F_2 + 2e^- \rightleftharpoons 2F^- \qquad E^{\ominus} = +2.87 \text{ V}$

The reverse reaction must be written to show oxidation: $2F^- \rightarrow F_2 + 2e^$ unlikely to happen



- At the anode, oxidation of the anions with the less positive (or more negative) E^{\ominus} will take place.
- Example 6: The chemical species present in the electrolyte are Cl⁻ and H₂O.

 $Cl_2 + 2e^- \rightleftharpoons 2Cl^- E^{\ominus} = +1.36 V$

 $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \quad E^{\ominus} = +1.23 \text{ V}$

Since H₂O is lower in the electrochemical series than Cl^- (*i.e.* $E^{\ominus}(O_2 | H_2O)$) is less positive or more negative than $E^{\ominus}(Cl_2 | Cl^-)$), H₂O has a higher tendency to be oxidised than Cl^- so H_2O is preferentially oxidised at the anode, resulting in the effervescence of oxygen gas.

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



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- ***** Factors Affecting Selective Discharge:
- (b) Concentration of the ion present in the electrolyte (because the concentration of the electrolyte affects standard electrode potentials).
 - *Higher concentration* of an ion makes it *easier / more likely to be selectively discharged*.

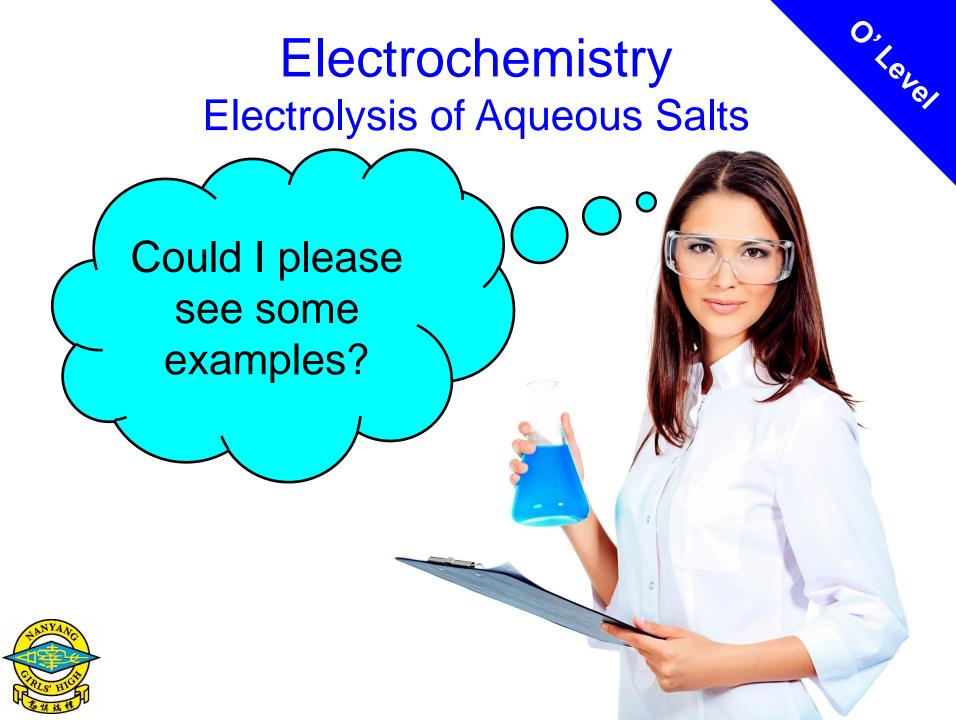


- Example 7: Consider the electrolysis of concentrated NaCl(aq) (brine) using inert electrodes. Both Cl⁻ and H₂O present in the brine are attracted towards the anode.
- H₂O should be preferentially oxidised, but because there is a high concentration of C*l*⁻ in the brine, C*l*⁻ is preferentially oxidised at the anode. The difference between the *E*[⊖] values of C*l*⁻ and H₂O is small, and the effect of the high concentration of C*l*⁻ is sufficient for C*l*⁻ to be preferentially oxidised.

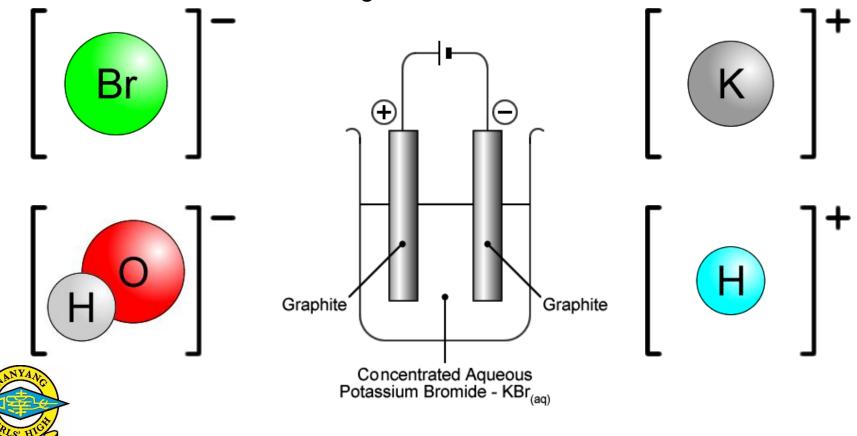
 $Cl_2 + 2e^- \rightleftharpoons 2Cl^- E^{\ominus} = +1.36 V$

- $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \quad E^{\ominus} = +1.23 \text{ V}$
 - At the anode, Cl^- is oxidised to Cl_2 : $2Cl^- \rightarrow Cl_2 + 2e^-$

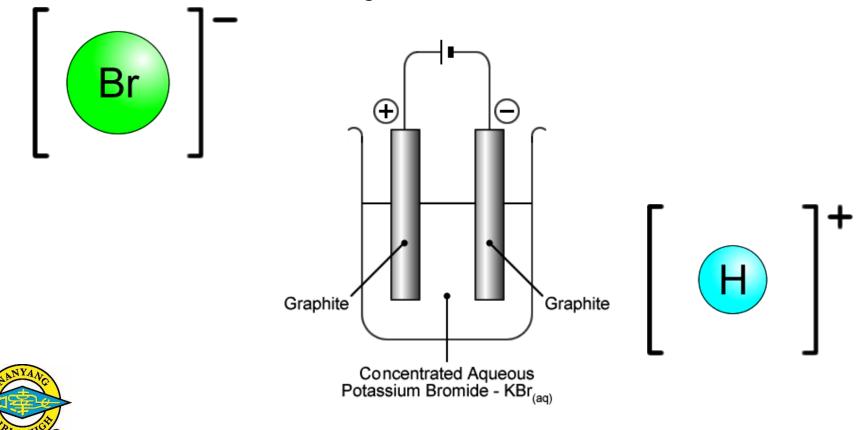




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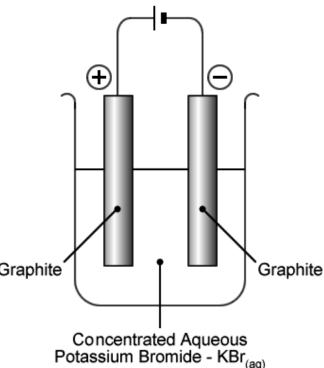
using inert electrodes?

a) At the anode (+ve):

Negatively charged bromide ions and hydroxide ions (anions) are both attracted to the positive anode.

At high concentration, bromide ions are preferentially oxidised to molecular bromine at the anode:

 $2Br^{-}(aq) \rightarrow Br_{2}(aq) + 2e^{-}$ Graphite



b) At the *cathode* (-ve):

Positively charged potassium ions and hydrogen ions (cations) are both attracted to the negative cathode.

Potassium is above hydrogen in the electrochemical series, therefore hydrogen ions are preferentially reduced to molecular hydrogen at the cathode:

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



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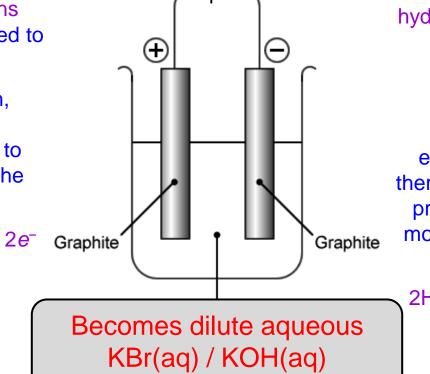
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Electrochemistry Electrolysis of Aqueous Electrolytes At the Cathode: More positive / less negative E^{\ominus} is preferentially reduced.

 $K^{+} + e^{-} \rightleftharpoons K \quad E^{\ominus} = -2.92 V$ 2H₂O + 2e⁻ ⇒ H₂ + 2OH⁻ $E^{\ominus} = -0.83 V$ 2H₂O + 2e⁻ → H₂ + 2OH⁻

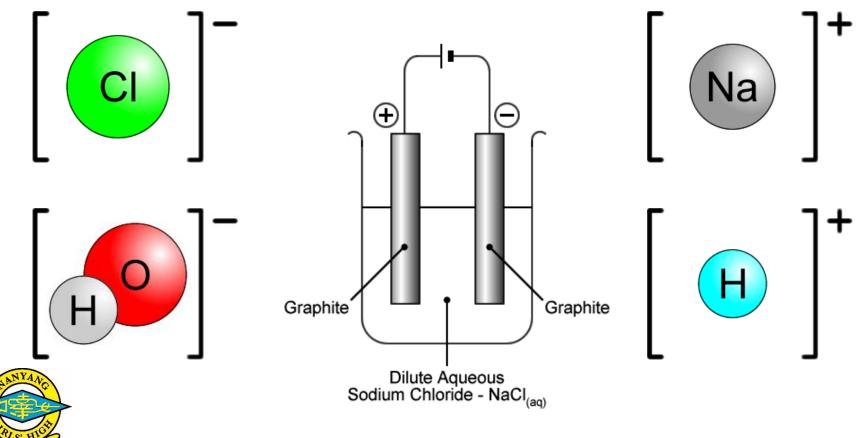
At the Anode

More negative / less positive E^{\ominus} is preferentially oxidised. More concentrated is preferentially oxidised. $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $E^{\ominus} = +1.23 \text{ V}$ $Br_2 + 2e^- \rightleftharpoons 2Br^ E^{\ominus} = +1.07 \text{ V}$ $2Br^- \rightarrow Br_2 + 2e^-$

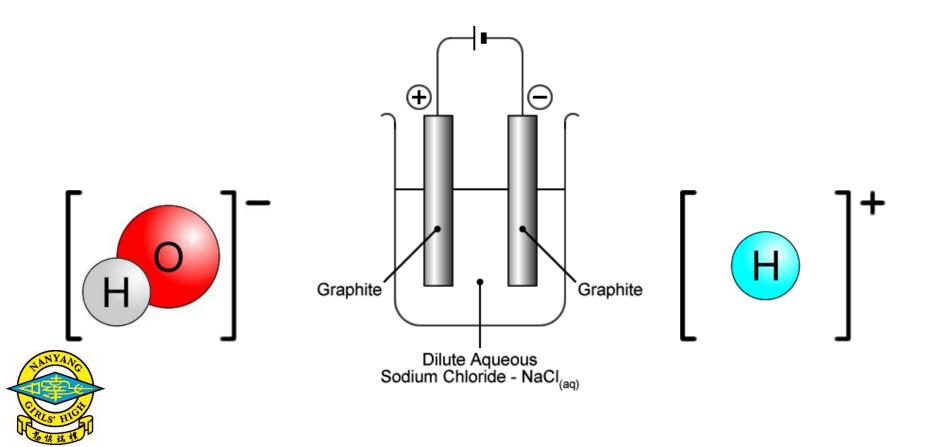


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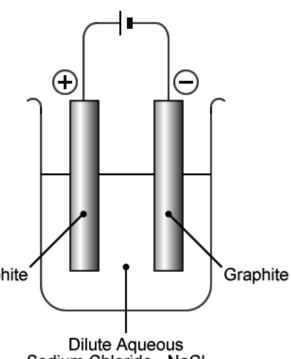
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a) At the anode (+ve):

Negatively charged chloride ions and hydroxide ions (anions) are both attracted to the positive anode.

Because the solution is dilute, hydroxide ions are preferentially oxidised to molecular oxygen and water at the anode:

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



Sodium Chloride - NaCl(aq)

b) At the *cathode* (–*ve*):

Positively charged sodium ions and hydrogen ions (cations) are both attracted to the negative cathode.

Sodium is above hydrogen in the electrochemical series, therefore hydrogen ions are preferentially reduced to molecular hydrogen at the cathode:

 $2H^+(aq) + 2e^- \rightarrow H_2(q)$



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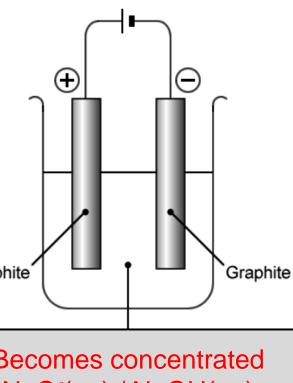
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electrodes?



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Becomes concentrated NaCl(aq) / NaOH(aq)

Electrochemistry Electrolysis of Aqueous Electrolytes At the Cathode: More positive / less negative E^{\ominus} is preferentially reduced. Na⁺ + e⁻ \rightleftharpoons Na $E^{\ominus} = -2.71$ V $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^- E^{\ominus} = -0.83$ V $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

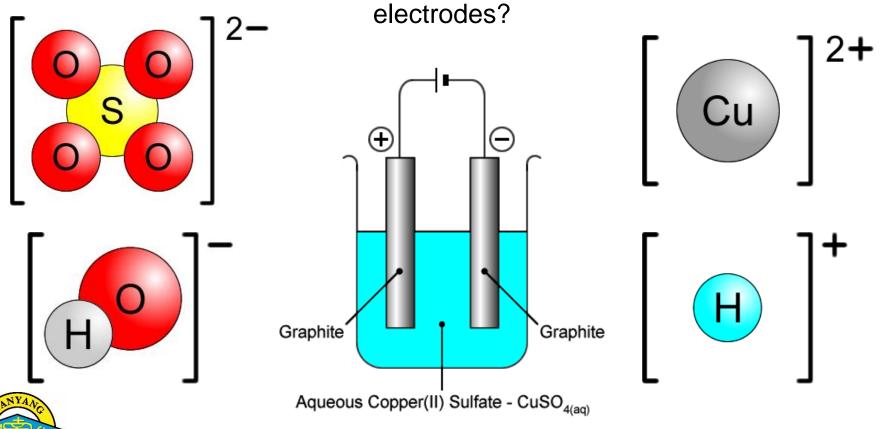
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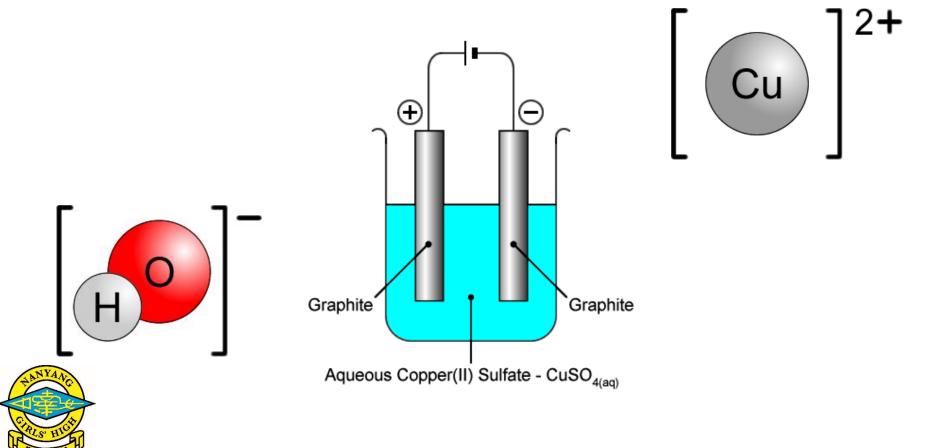


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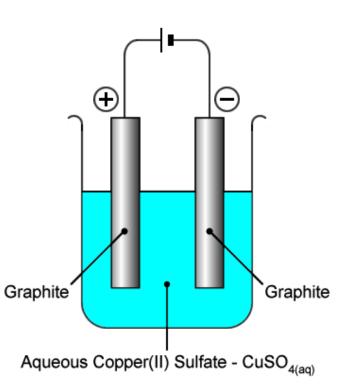


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a) At the anode (+ve):

Negatively charged sulfate ions and hydroxide ions (anions) are both attracted to the positive anode. Regardless of concentration, sulfate ions are not oxidised during electrolysis. Consequently, hydroxide ions are preferentially oxidised to molecular oxygen and water at the anode: $4OH^{-}(aq) \rightarrow O_{2}(g) + 2H_{2}O(l) + 4e^{-1}$



b) At the *cathode (-ve)*:

Positively charged copper(II) ions and hydrogen ions (cations) are both attracted to the negative cathode.

Copper is below hydrogen in the electrochemical series, therefore copper(II) ions are preferentially reduced to copper atoms at the cathode:

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

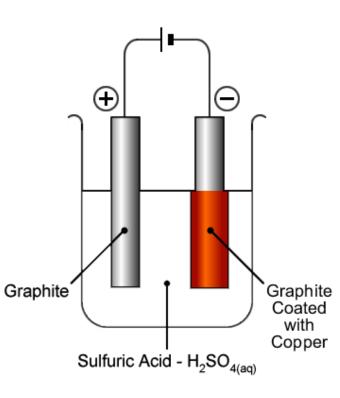


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Electrochemistry Electrolysis of Aqueous Electrolytes

At the Cathode:

More positive / less negative E^{\ominus} is preferentially reduced. $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^- \qquad E^{\ominus} = -0.83 \text{ V}$ $Cu^{2+} + 2e^- \rightleftharpoons Cu \qquad E^{\ominus} = +0.34 \text{ V}$ $Cu^{2+} + 2e^- \rightarrow Cu$

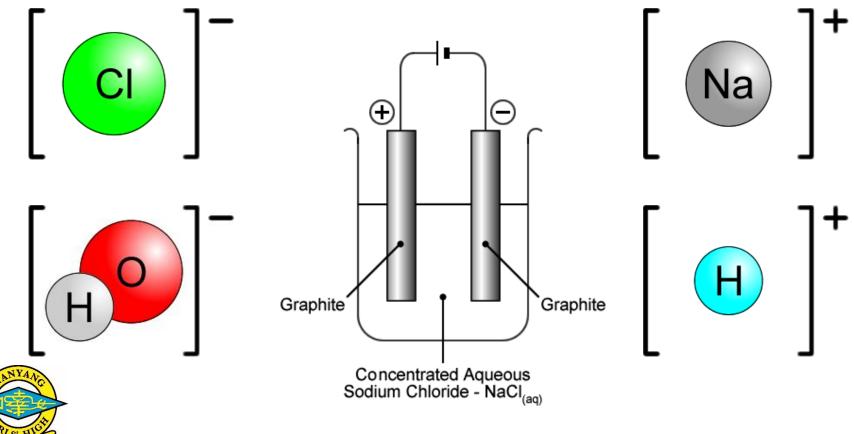
At the Anode

More negative / less positive E^{\ominus} is preferentially oxidised. More concentrated is preferentially oxidised. $S_2O_8^{2-} + 2e^- \Rightarrow 2SO_4^{2-}$ $E^{\ominus} = +2.01 \text{ V}$ $O_2 + 4H^+ + 4e^- \Rightarrow 2H_2O$ $E^{\ominus} = +1.23 \text{ V}$ $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

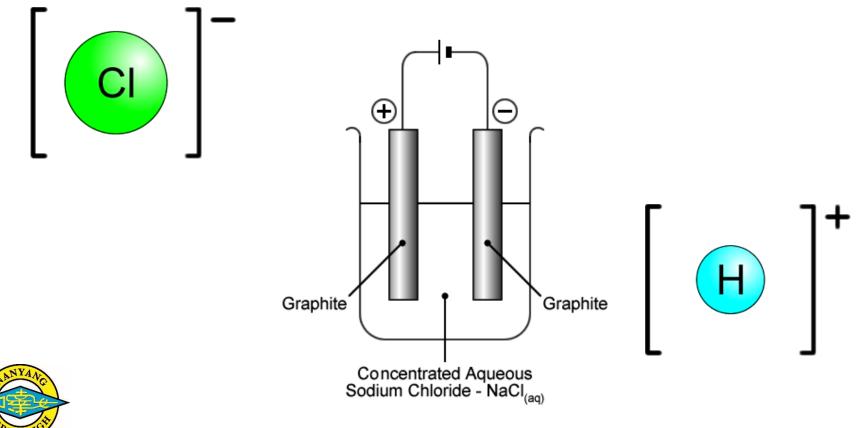


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• What products are formed at **a**) the anode and **b**) the cathode when *concentrated aqueous sodium chloride* is electrolysed using inert electrodes?



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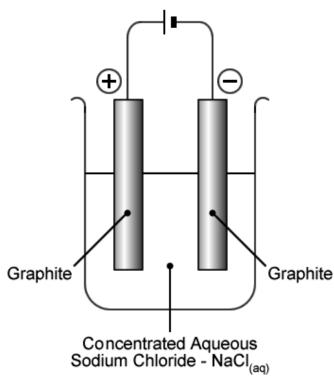
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a) At the anode (+ve):

Negatively charged chloride ions and hydroxide ions (anions) are both attracted to the positive anode.

At high concentration, chloride ions are preferentially oxidised to molecular chlorine at the anode:

 $2Cl^{-}(aq) \rightarrow Cl_{2}(g) + 2e^{-}$



b) At the *cathode* (-ve):

Positively charged sodium ions and hydrogen ions (cations) are both attracted to the negative cathode.

Sodium is above hydrogen in the electrochemical series, therefore hydrogen ions are preferentially reduced to molecular hydrogen at the cathode:

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



• What products are formed at **a**) the anode and **b**) the cathode when *concentrated aqueous sodium chloride* is electrolysed using inert electrodes?

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At high concentration, chloride ions are preferentially oxidised to molecular chlorine at the anode:

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Graphite Becomes dilute aqueous

NaCl(aq) / NaOH(aq)

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Positively charged sodium ions and hydrogen ions (cations) are both attracted to the negative cathode.

Sodium is above hydrogen in the electrochemical series, therefore hydrogen ions are preferentially reduced to molecular hydrogen at the cathode:

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Electrochemistry Electrolysis of Aqueous Electrolytes At the Cathode: More positive / less negative E^{\ominus} is preferentially reduced. $Na^{+} + e^{-} \rightleftharpoons Na \quad E^{\ominus} = -2.71 \vee$ $2H_2O + 2e^{-} \rightleftharpoons H_2 + 2OH^{-} \quad E^{\ominus} = -0.83 \vee$ $2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$

At the Anode

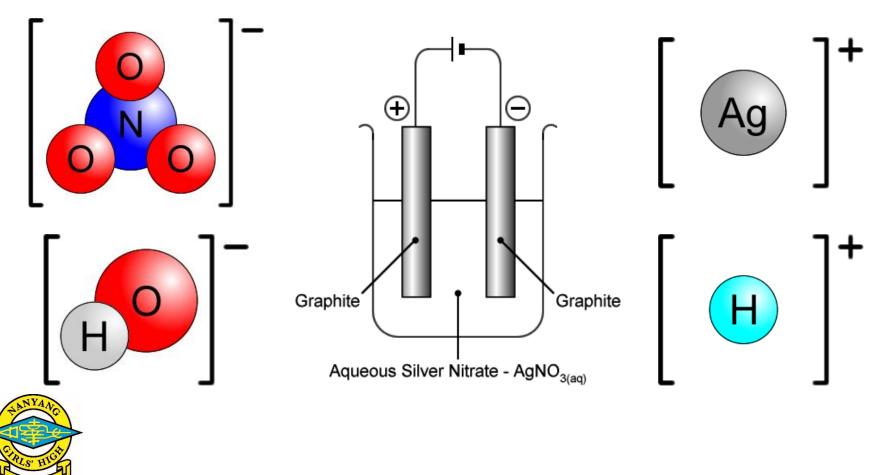
More negative / less positive E^{\ominus} is preferentially oxidised. More concentrated is preferentially oxidised. $Cl_{\circ} + 2e^{-} \Rightarrow 2Cl^{-}$ $E^{\ominus} = +1.36$ V

$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \qquad E^{\ominus} = +1.23 V$$
$$2Cl^- \rightarrow Cl_2 + 2e^-$$

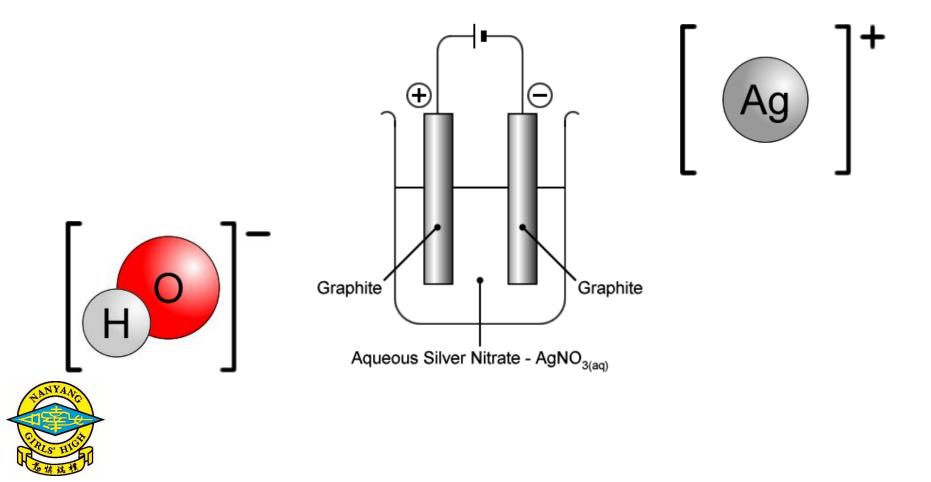


• New Integrated Programme 2025 – to align with A' Level Chemistry.

• What products are formed at **a**) the anode and **b**) the cathode when *aqueous silver nitrate* is electrolysed using inert electrodes?



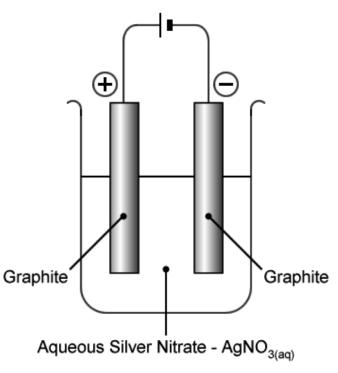
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• What products are formed at **a**) the anode and **b**) the cathode when *aqueous silver nitrate* is electrolysed using inert electrodes?

a) At the anode (+ve):

Negatively charged nitrate ions and hydroxide ions (anions) are both attracted to the positive anode. Regardless of concentration, nitrate ions are not oxidised during electrolysis. Consequently, hydroxide ions are preferentially oxidised to molecular oxygen and water at the anode: $4OH^{-}(aq) \rightarrow O_{2}(g) + 2H_{2}O(l) + 4e^{-1}$



b) At the *cathode* (-ve):

Positively charged silver ions and hydrogen ions (cations) are both attracted to the negative cathode.

Silver is below hydrogen in the electrochemical series, therefore silver ions are preferentially reduced to silver atoms at the cathode:

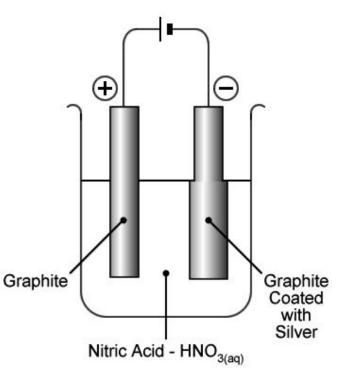
Ag⁺(aq) + $e^- \rightarrow$ Ag(s)



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Negatively charged nitrate ions and hydroxide ions (anions) are both attracted to the positive anode. Regardless of concentration, nitrate ions are not oxidised during electrolysis. Consequently, hydroxide ions are preferentially oxidised to molecular oxygen and water at the anode: $4OH^{-}(aq) \rightarrow O_{2}(g) + 2H_{2}O(l) + 4e^{-1}$



b) At the *cathode (-ve)*:

Positively charged silver ions and hydrogen ions (cations) are both attracted to the negative cathode.

Silver is below hydrogen in the electrochemical series, therefore silver ions are preferentially reduced to silver atoms at the cathode:

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



Electrochemistry Electrolysis of Aqueous Electrolytes

At the Cathode:

More positive / less negative E^{\ominus} is preferentially reduced. $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^- \quad E^{\ominus} = -0.83 \text{ V}$ $Ag^+ + e^- \rightleftharpoons Ag \quad E^{\ominus} = +0.80 \text{ V}$ $Ag^+ + e^- \rightarrow Ag$

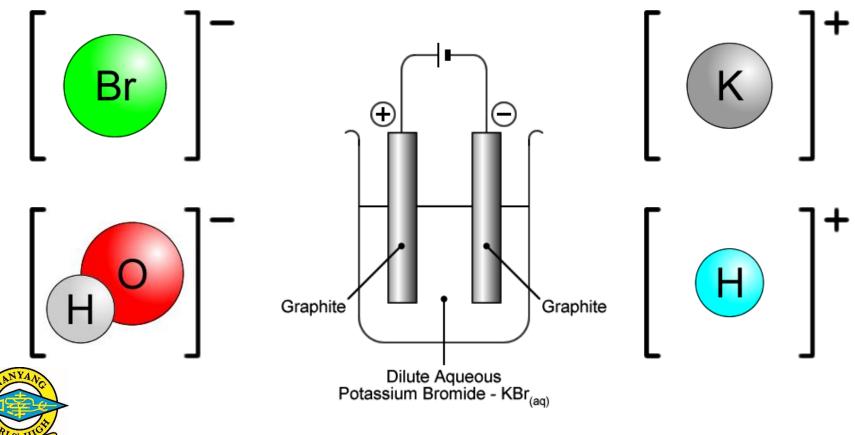
At the Anode

More negative / less positive E^{\ominus} is preferentially oxidised. More concentrated is preferentially oxidised. $O_2 + 4H^+ + 4e^- \Rightarrow 2H_2O \qquad E^{\ominus} = +1.23 \text{ V}$ $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

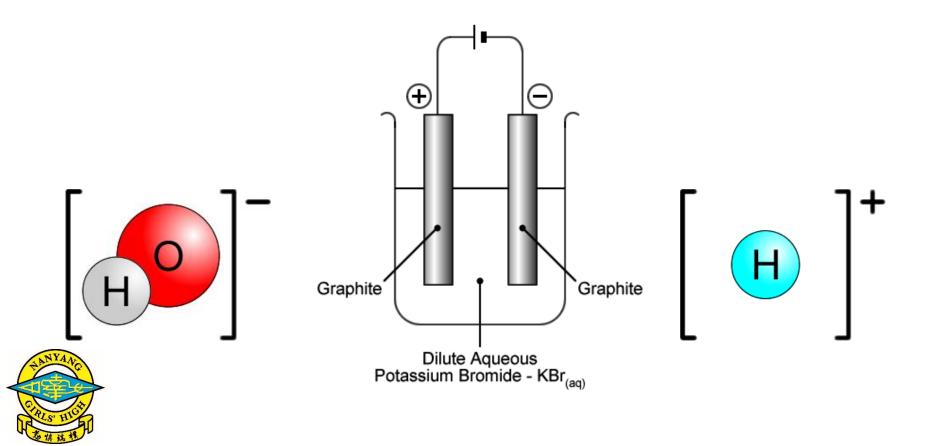


• New Integrated Programme 2025 – to align with A' Level Chemistry.

• What products are formed at **a**) the anode and **b**) the cathode when *dilute aqueous potassium bromide* is electrolysed using inert electrodes?



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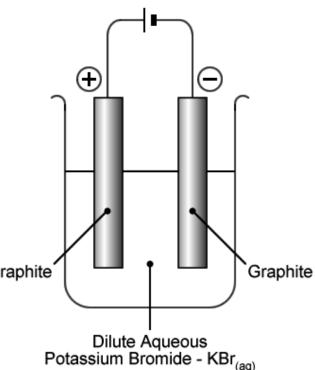
• What products are formed at **a**) the anode and **b**) the cathode when *dilute aqueous potassium bromide* is electrolysed using inert electrodes?

a) At the anode (+ve):

Negatively charged bromide ions and hydroxide ions (anions) are both attracted to the positive anode.

Because the solution is dilute, hydroxide ions are preferentially oxidised to molecular oxygen and water at the anode:

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



b) At the *cathode (-ve)*:

Positively charged potassium ions and hydrogen ions (cations) are both attracted to the negative cathode.

Potassium is above hydrogen in the electrochemical series, therefore hydrogen ions are preferentially reduced to molecular hydrogen at the cathode:

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

(+)Graphite Becomes concentrated KBr(aq) / KOH(aq)

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Positively charged potassium ions and hydrogen ions (cations) are both attracted to the negative cathode.

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Electrochemistry Electrolysis of Aqueous Electrolytes At the Cathode: More positive / less negative E^{\ominus} is preferentially reduced.

 $K^{+} + e^{-} \rightleftharpoons K \quad E^{\ominus} = -2.92 V$ 2H₂O + 2e⁻ ⇒ H₂ + 2OH⁻ $E^{\ominus} = -0.83 V$ 2H₂O + 2e⁻ → H₂ + 2OH⁻

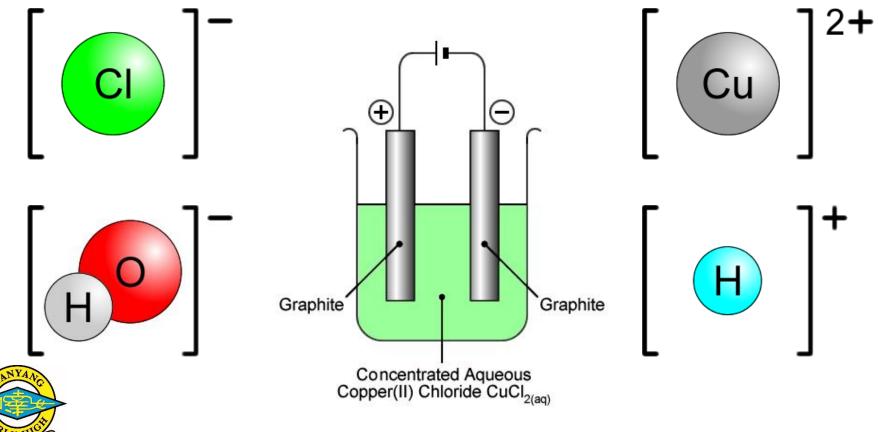
At the Anode

More negative / less positive E^{\ominus} is preferentially oxidised. More concentrated is preferentially oxidised. $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $E^{\ominus} = +1.23 \text{ V}$ $Br_2 + 2e^- \rightleftharpoons 2Br^ E^{\ominus} = +1.07 \text{ V}$ $2Br^- \rightarrow Br_2 + 2e^-$

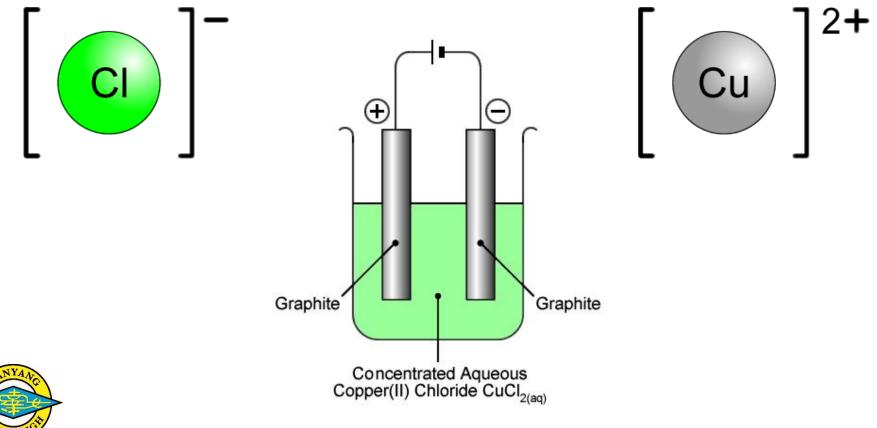


• New Integrated Programme 2025 – to align with A' Level Chemistry.

• What products are formed at **a**) the anode and **b**) the cathode when *concentrated aqueous copper(II) chloride* is electrolysed using inert electrodes?



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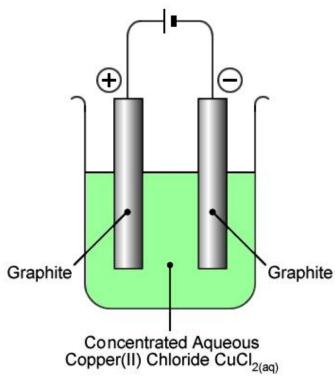
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a) At the anode (+ve):

Negatively charged chloride ions and hydroxide ions (anions) are both attracted to the positive anode.

At high concentration, chloride ions are preferentially oxidised to molecular chlorine at the anode:

 $2Cl^{-}(aq) \rightarrow Cl_{2}(g) + 2e^{-}$



b) At the *cathode (-ve)*:

Positively charged copper(II) ions and hydrogen ions (cations) are both attracted to the negative cathode.

Copper is below hydrogen in the electrochemical series, therefore copper(II) ions are preferentially reduced to copper atoms at the cathode:

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



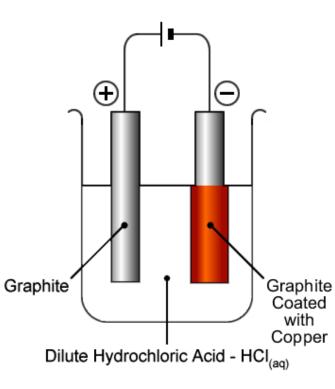
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Electrochemistry Electrolysis of Aqueous Electrolytes

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At the Anode

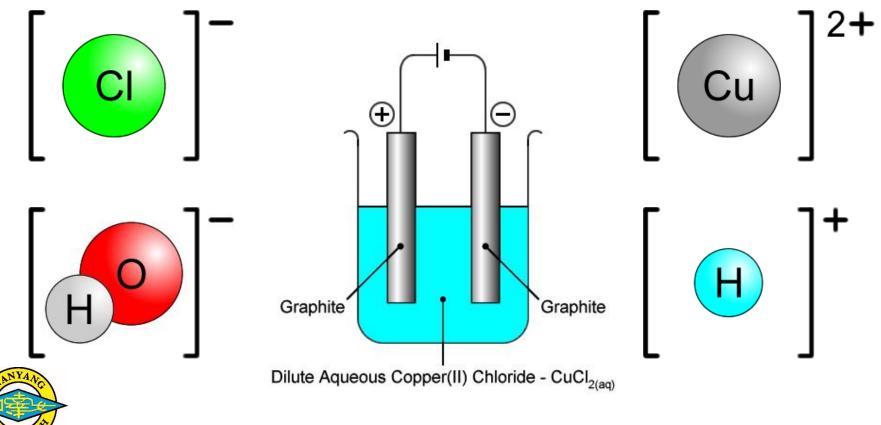
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 $2Cl^{-} \rightarrow Cl_2 + 2e^{-}$

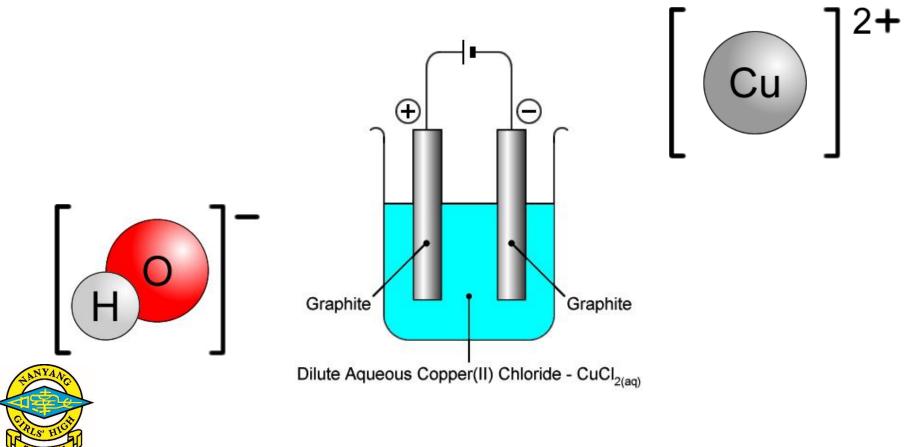


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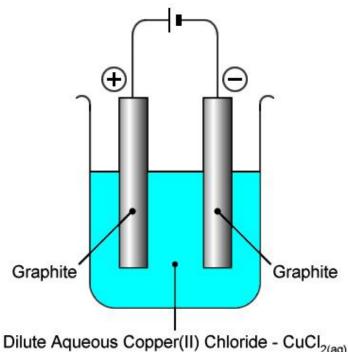
a) At the anode (+ve):

Negatively charged chloride ions and hydroxide ions (anions) are both attracted to the positive anode.

Because the solution is dilute, hydroxide ions are preferentially oxidised to molecular oxygen at the anode:

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

electrodes?



b) At the *cathode* (-ve):

Positively charged copper(II) ions and hydrogen ions (cations) are both attracted to the negative cathode.

Copper is below hydrogen in the electrochemical series, therefore copper(II) ions are preferentially reduced to copper atoms at the cathode:

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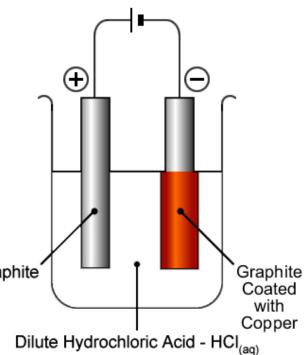
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Electrochemistry Electrolysis of Aqueous Electrolytes

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More positive / less negative E^{\ominus} is preferentially reduced. $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^- \qquad E^{\ominus} = -0.83 \text{ V}$ $Cu^{2+} + 2e^- \rightleftharpoons Cu \qquad E^{\ominus} = +0.34 \text{ V}$ $Cu^{2+} + 2e^- \rightarrow Cu$

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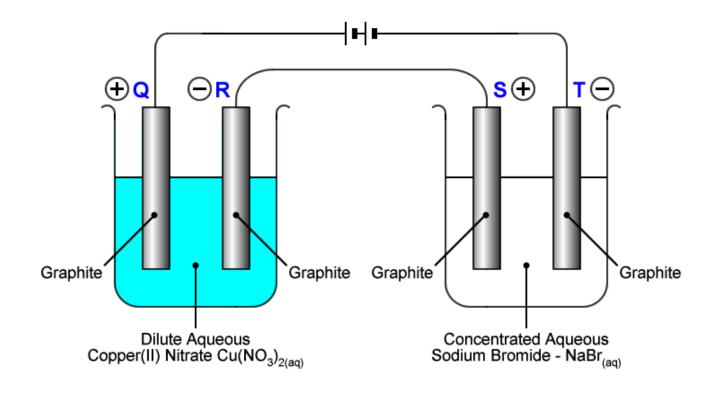
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• New Integrated Programme 2025 – to align with A' Level Chemistry.

O. Folor

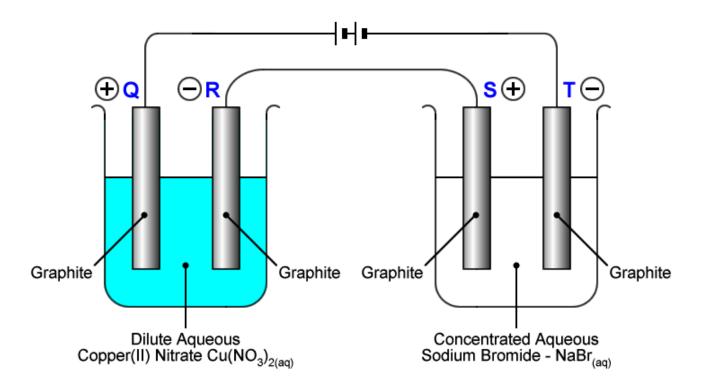
 What products are formed at the electrodes Q, R, S, and T when the following system is electrolysed using inert electrodes?





Tele!

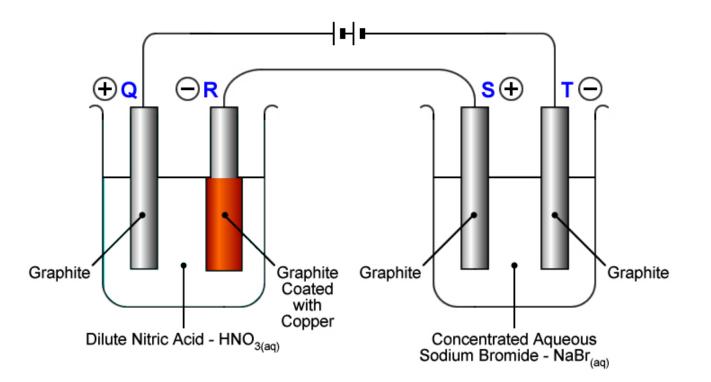
Q: 4OH⁻(aq) → O₂(g) + 2H₂O(l) + 4e⁻ R: Cu²⁺(aq) + 2e⁻ → Cu(s) S: 2Br⁻(aq) → Br₂(aq) + 2e⁻ T: 2H⁺(aq) + 2e⁻ → H₂(g)





O. Ler

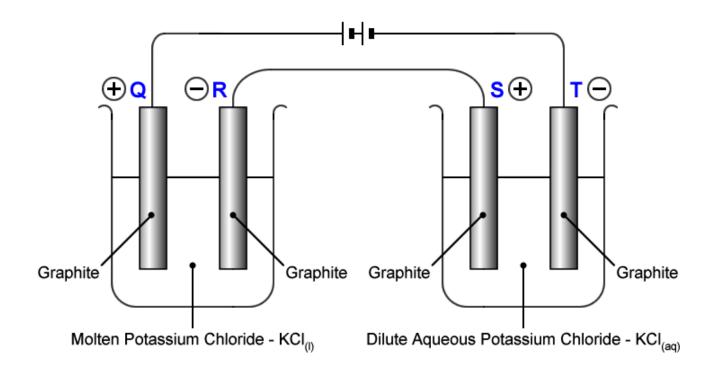
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O, Feler

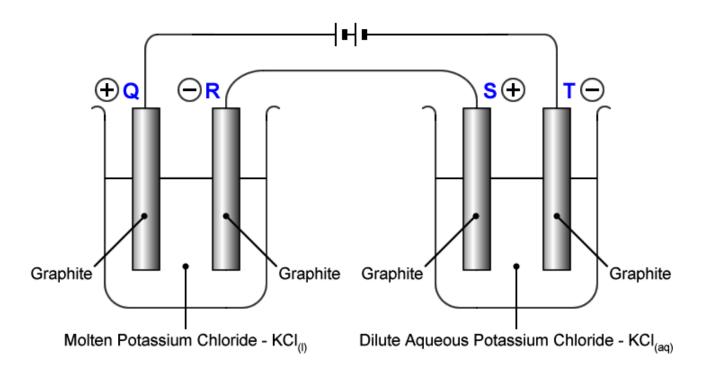
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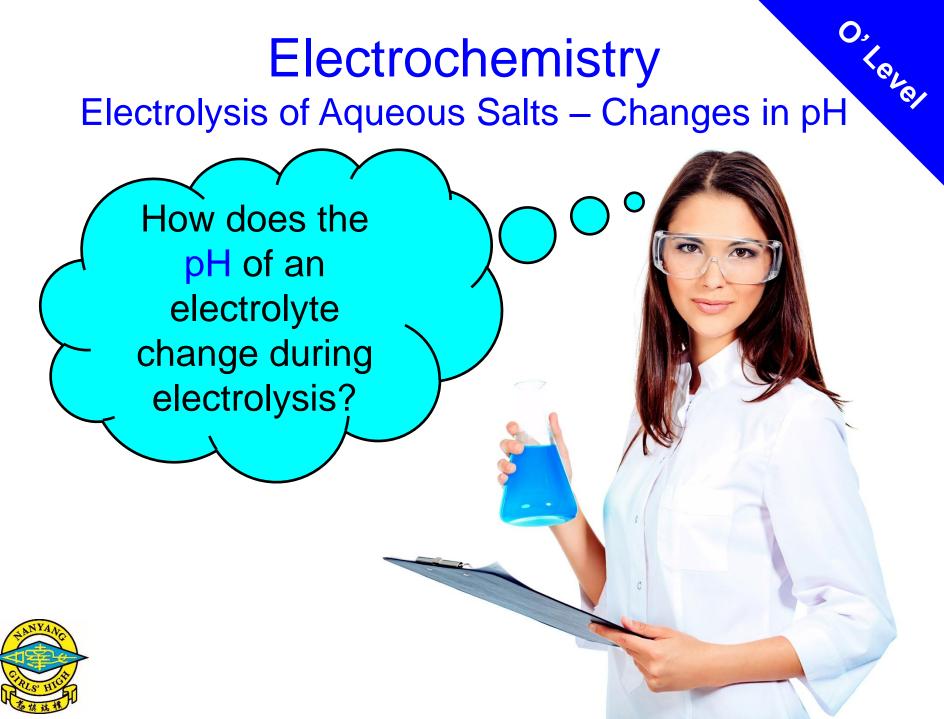


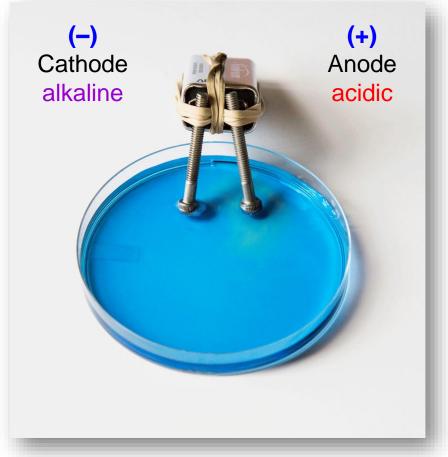
O. Ler

 $\begin{array}{l} \textbf{Q: } 2Cl^-(l) \rightarrow Cl_2(g) + 2e^- \quad \textbf{R: } \mathsf{K}^+(l) + e^- \rightarrow \mathsf{K}(l) \\ \textbf{S: } 4OH^-(aq) \rightarrow O_2(g) + 2\mathsf{H}_2\mathsf{O}(l) + 4e^- \quad \textbf{T: } 2\mathsf{H}^+(aq) + 2e^- \rightarrow \mathsf{H}_2(g) \end{array}$











• The indicator bromothymol blue is yellow below pH 6.

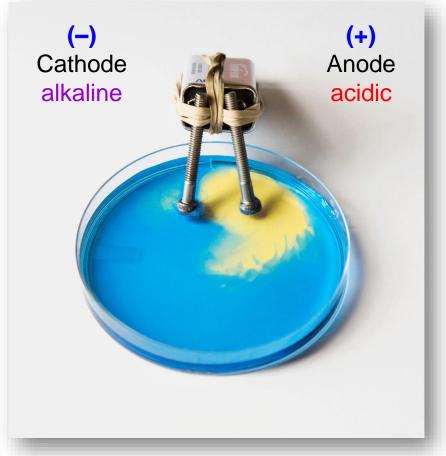
Anode (+)

Water Dissociates $4H_2O(l) \rightarrow 4H^+(aq) + 4OH^-(aq)$

Hydroxide Ions are Oxidised $4OH^{-}(aq) \rightarrow O_{2}(g) + 2H_{2}O(l) + 4e^{-}$

 As OH⁻(aq) are oxidised, the concentration of the OH⁻(aq) at the anode decreases.

• The 4H⁺(aq) that are not reduced will make the solution at the anode *acidic* (pH < 7).



CALS' HICK

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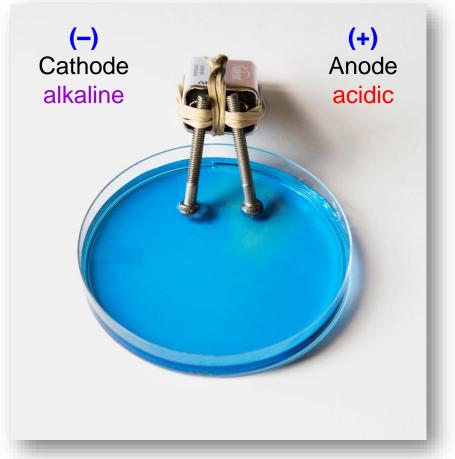
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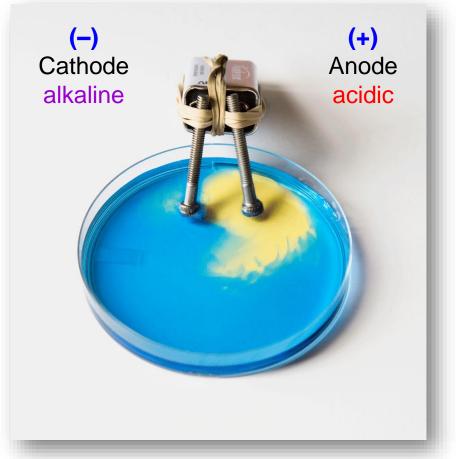
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Water Dissociates $2H_2O(l) \rightarrow 2H^+(aq) + 2OH^-(aq)$

Hydrogen Ions are Reduced $2H^+(aq) + 2e^- \rightarrow H_2(g)$

 As H⁺(aq) are reduced, the concentration of H⁺(aq) at the cathode decreases.

 The 2OH⁻(aq) that are not oxidised will make the solution at the cathode *alkaline* (pH > 7).





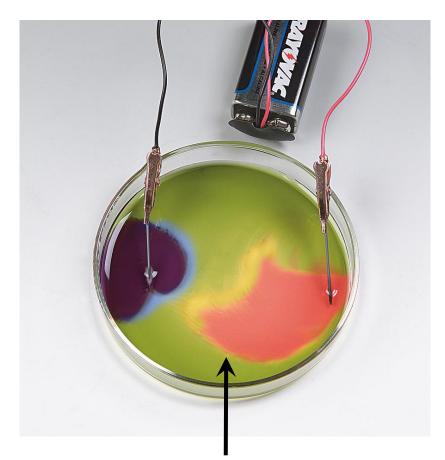
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 As H⁺(aq) are reduced, the concentration of H⁺(aq) at the cathode decreases.

 The 2OH⁻(aq) that are not oxidised will make the solution at the cathode *alkaline* (pH > 7).

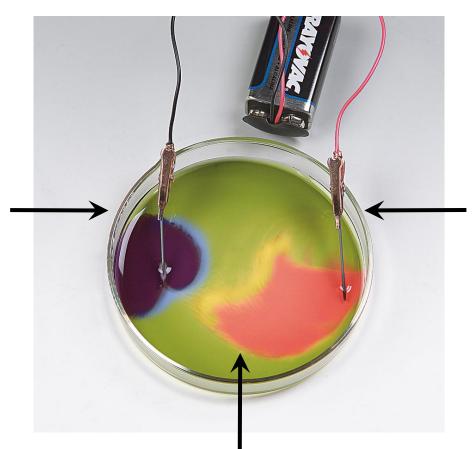




 Electrolyte with Universal Indicator added.
GREEN = neutral (pH = 7)

Electrochemistry Electrolysis of Aqueous Salts – Changes in pH

 Cathode (–) $H^+(aq)$ are reduced. The remaining OH⁻(aq) ions cause the solution to become *alkaline* (pH > 7) causing the Universal Indicator to turn BLUE.



Anode (+)

OH⁻(aq) are oxidised. The remaining H⁺(aq) ions cause the solution to become *acidic* (pH < 7) causing the Universal Indicator to turn **RED**.



 Electrolyte with Universal Indicator added.
GREEN = neutral (pH = 7)

Electrochemistry

Electrolysis of Aqueous Salts – Changes in pH

At the Cathode:

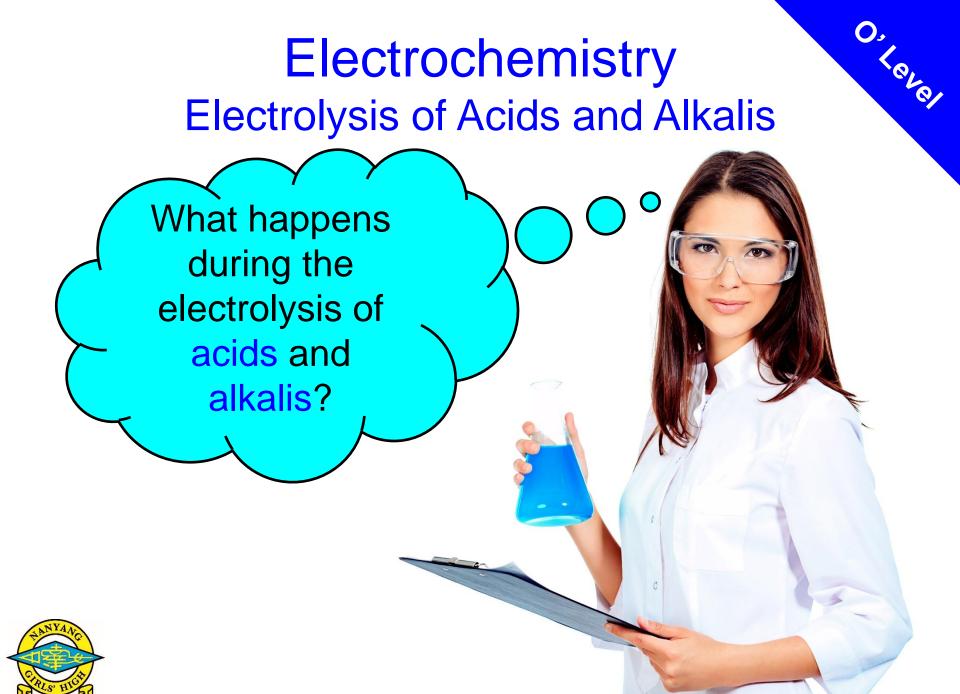
 $2H_2O + 2e^- \Rightarrow H_2 + 2OH^- \quad E^{\ominus} = -0.83 V$ Water is reduced, forming hydroxide ions which make the solution alkaline and turns the universal indicator blue / purple. $2H_2O + 2e^- \Rightarrow H_2 + 2OH^-$

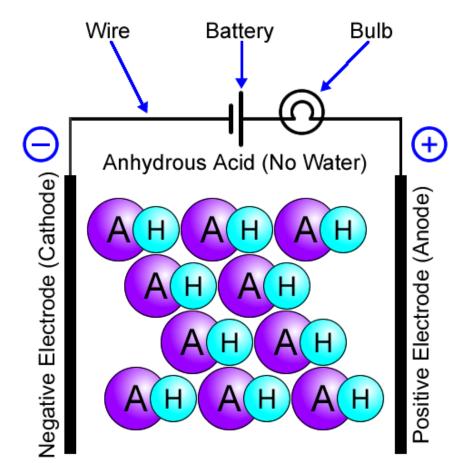
At the Anode

 $O_2 + 4H^+ + 4e^- \Rightarrow 2H_2O$ *E*[⊖] = +1.23 V Water is oxidised, forming hydrogen ions which make the solution acidic and turns the universal indicator red. $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$



• New Integrated Programme 2025 – to align with A' Level Chemistry.

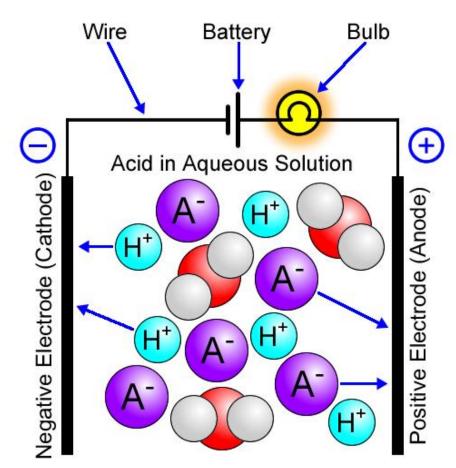




 A pure acid, one that has not dissolved in water, will be composed only of simple covalent molecules. There are no mobile ions to serve as charge carrying particles. The pure acid is an electrical insulator.

Fel e

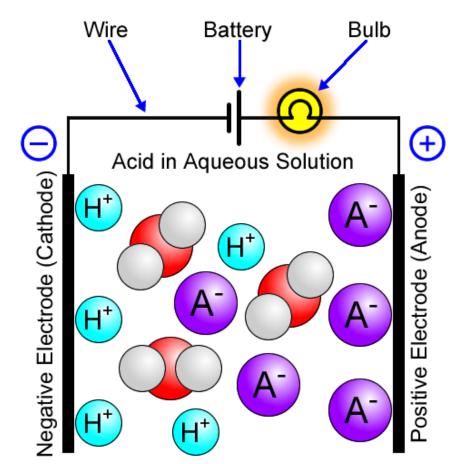




 Once dissolved in water, the acid will *ionize* to form positively charged hydrogen ions and anions. The ions are free to move throughout the solution and therefore serve as mobile charge carrying particles.

- Lerel



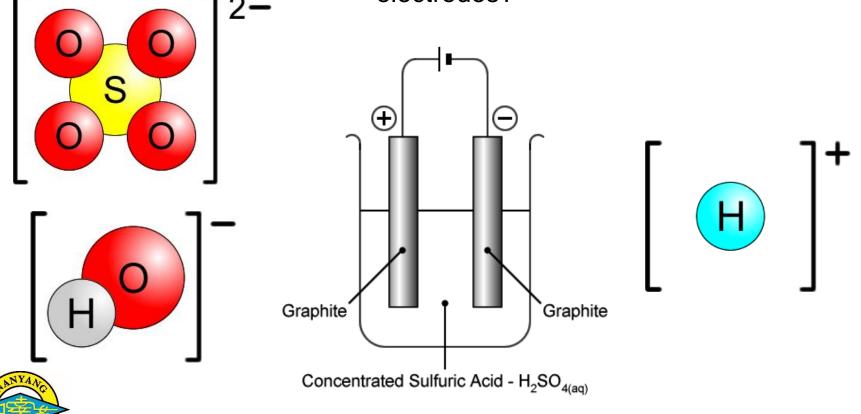


 When electrodes are inserted into the acidic solution, the *positively* charged hydrogen ions are attracted towards the cathode, while the anions are attracted towards the anode. The movement of ions towards the electrode of opposite charge constitutes the flow of electricity.

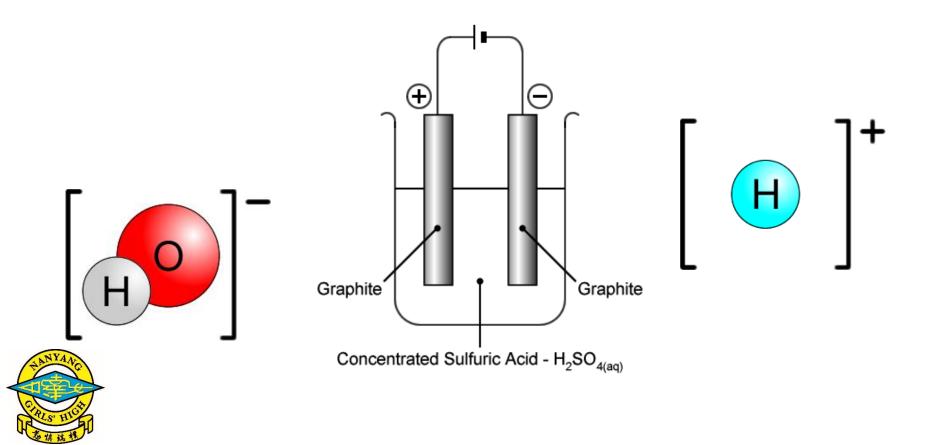


 What products are formed at a) the anode and b) the cathode when concentrated sulfuric acid is electrolysed using inert

electrodes?



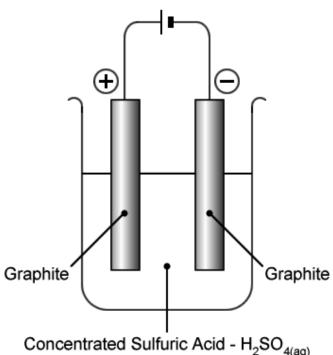
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• What products are formed at **a**) the anode and **b**) the cathode when *concentrated sulfuric acid* is electrolysed using inert electrodes?

a) At the anode (+ve):

Negatively charged sulfate ions and hydroxide ions (anions) are both attracted to the positive anode. Regardless of concentration, sulfate ions are not oxidised during electrolysis. Consequently, hydroxide ions are preferentially oxidised to molecular oxygen and water at the anode: $4OH^{-}(aq) \rightarrow O_2(g) + 2H_2O(l) + 4e^{-}$



b) At the *cathode* (–*ve*):

Hydrogen ions are the only cations present in the solution.

Positively charged hydrogen ions are attracted towards the negatively charged cathode where they are reduced to molecular hydrogen:

 $2H^+(aq) + 2e^- \rightarrow H_2(q)$



Electrochemistry Electrolysis of Aqueous Electrolytes

At the Cathode:

More positive / less negative E^{\ominus} is preferentially reduced. $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^- \qquad E^{\ominus} = -0.83 \text{ V}$ $2H^+ + 2e^- \rightleftharpoons H_2 \qquad E^{\ominus} = +0.00 \text{ V}$ $2H^+ + 2e^- \rightarrow H_2$

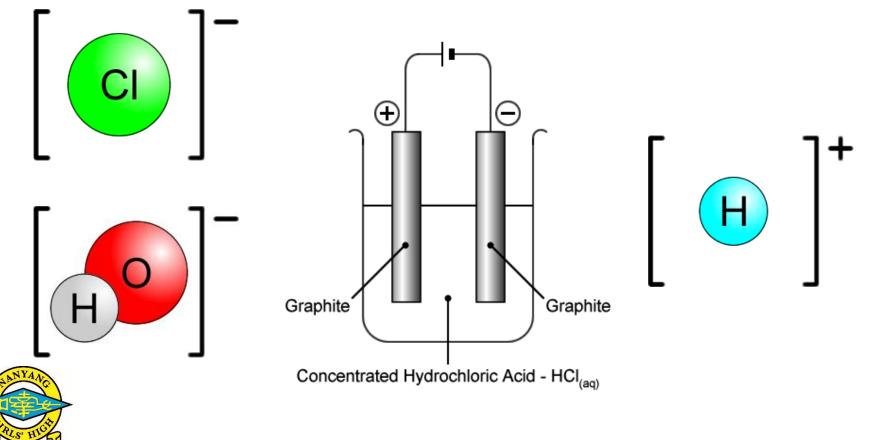
At the Anode

More negative / less positive E^{\ominus} is preferentially oxidised. More concentrated is preferentially oxidised. $S_2O_8^{2-} + 2e^- \Rightarrow 2SO_4^{2-}$ $E^{\ominus} = +2.01 \text{ V}$ $O_2 + 4H^+ + 4e^- \Rightarrow 2H_2O$ $E^{\ominus} = +1.23 \text{ V}$ $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

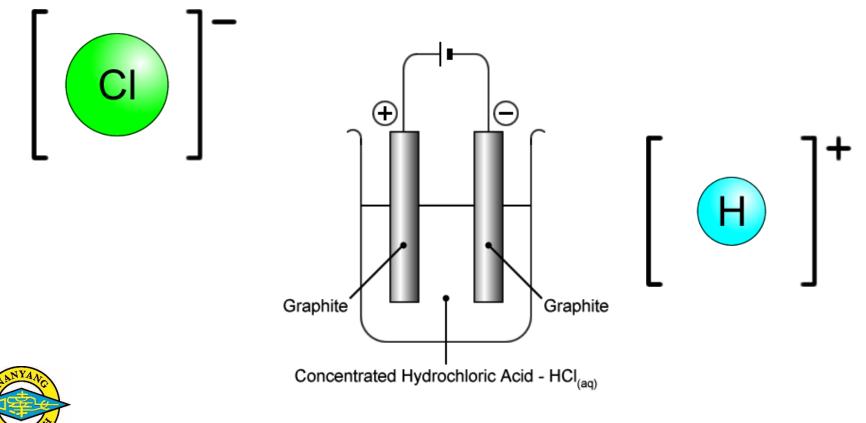


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 What products are formed at a) the anode and b) the cathode when concentrated hydrochloric acid is electrolysed using inert electrodes?



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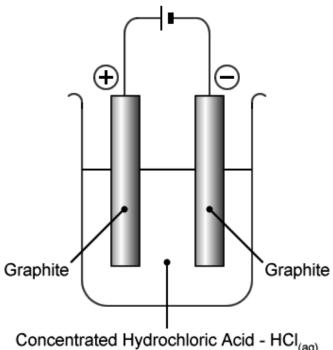
• What products are formed at **a**) the anode and **b**) the cathode when *concentrated hydrochloric acid* is electrolysed using inert electrodes?

a) At the anode (+ve):

Negatively charged chloride ions and hydroxide ions (anions) are both attracted to the positive anode.

At high concentration, chloride ions are preferentially oxidised to molecular chlorine at the anode:

 $2Cl^{-}(aq) \rightarrow Cl_{2}(g) + 2e^{-}$



b) At the *cathode* (–*ve*):

Hydrogen ions are the only cations present in the solution.

Positively charged hydrogen ions are attracted towards the negatively charged cathode where they are reduced to molecular hydrogen:

 $2H^+(aq) + 2e^- \rightarrow H_2(q)$



Electrochemistry Electrolysis of Aqueous Electrolytes

At the Cathode:

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At the Anode

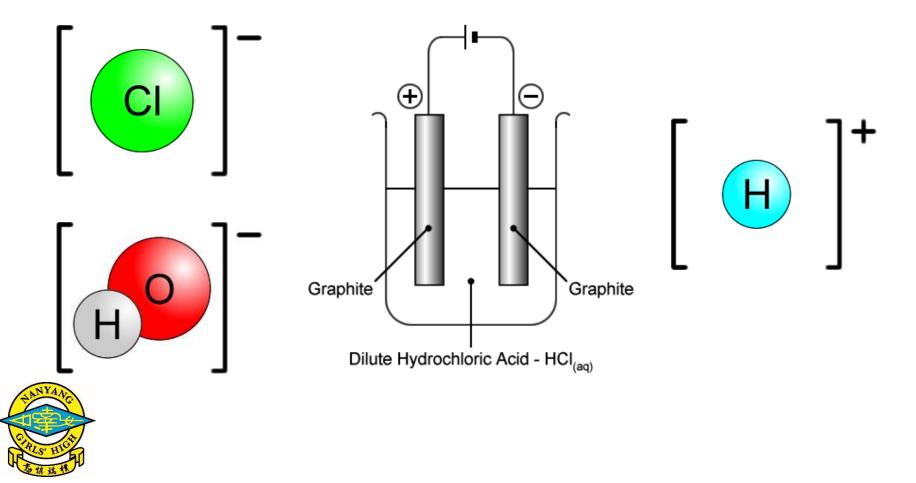
More negative / less positive E^{\ominus} is preferentially oxidised. More concentrated is preferentially oxidised. $Cl_2 + 2e^- \rightleftharpoons 2Cl^- \quad E^{\ominus} = +1.36 \text{ V}$ $O_2 + 4\text{H}^+ + 4e^- \rightleftharpoons 2\text{H}_2\text{O} \quad E^{\ominus} = +1.23 \text{ V}$

$$4\Pi' + 4e^{-} \approx 2\Pi_2 O \quad E^{\bigcirc} = +1.2$$
$$2Cl^{-} \rightarrow Cl_2 + 2e^{-}$$

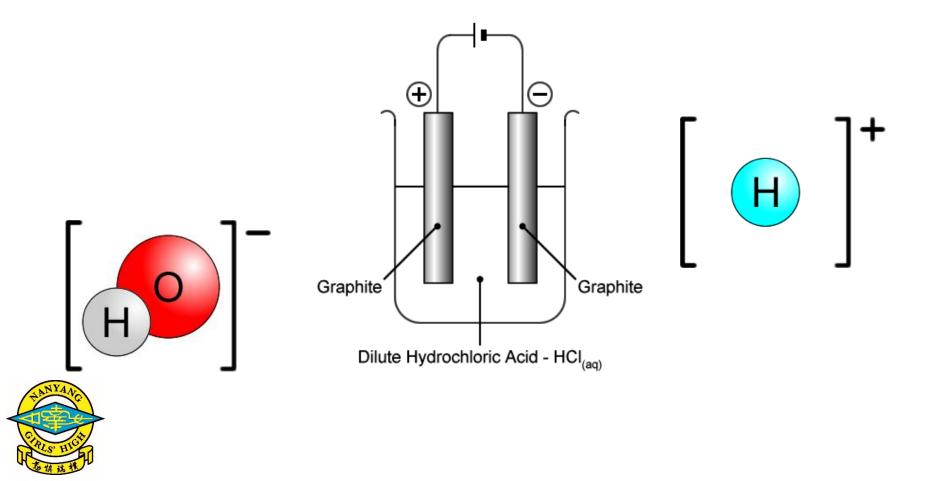


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• What products are formed at **a**) the anode and **b**) the cathode when *dilute hydrochloric acid* is electrolysed using inert electrodes?



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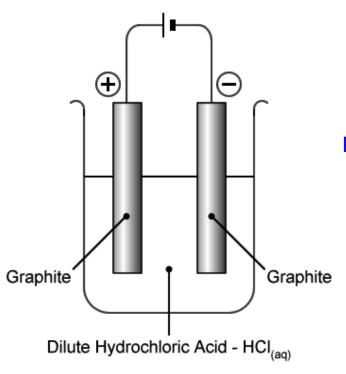
• What products are formed at **a**) the anode and **b**) the cathode when *dilute hydrochloric acid* is electrolysed using inert electrodes?

a) At the anode (+ve):

Negatively charged chloride ions and hydroxide ions (anions) are both attracted to the positive anode.

Because the solution is dilute, hydroxide ions are preferentially oxidised to molecular oxygen and water at the anode:

 $4OH^{-}(aq) \rightarrow O_{2}(g) + 2H_{2}O(l) + 4e^{-}$



b) At the *cathode (-ve)*:

Hydrogen ions are the only cations present in the solution.

Positively charged hydrogen ions are attracted towards the negatively charged cathode where they are reduced to molecular hydrogen:

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



Electrochemistry Electrolysis of Aqueous Electrolytes

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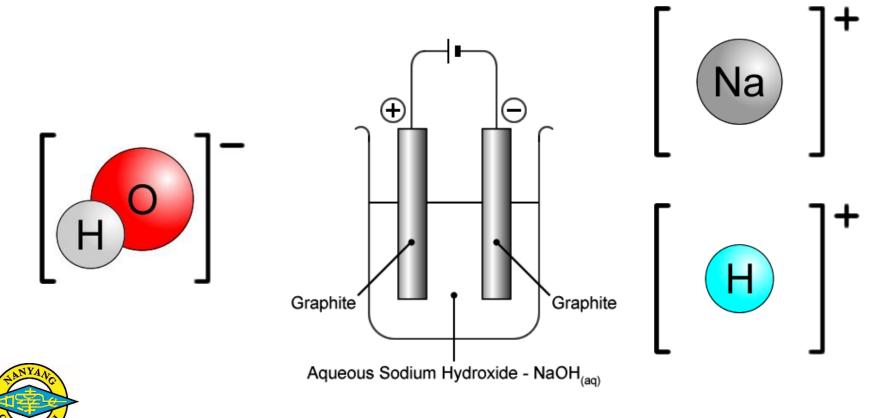
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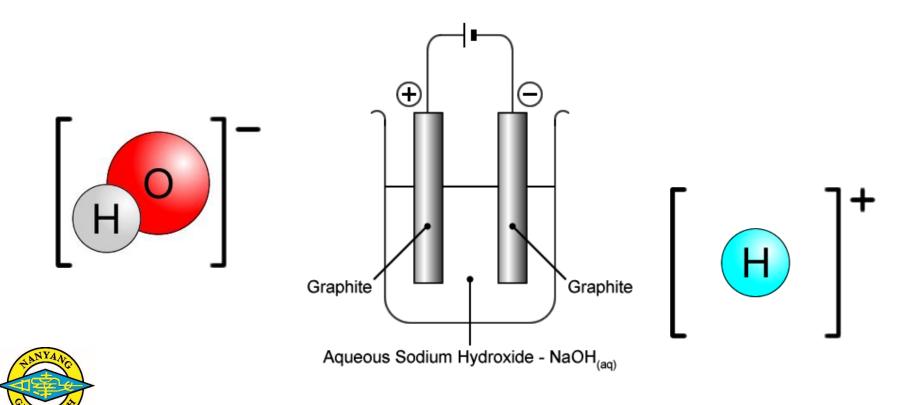


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 What products are formed at a) the anode and b) the cathode when aqueous sodium hydroxide is electrolysed using inert electrodes?



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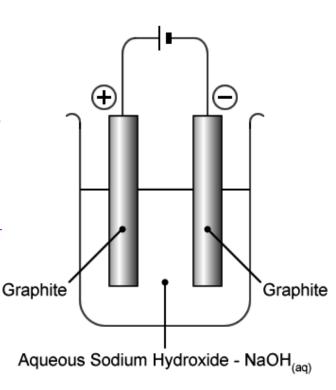
 What products are formed at a) the anode and b) the cathode when aqueous sodium hydroxide is electrolysed using inert electrodes?

a) At the anode (+ve):

Hydroxide ions are the only anions present in the solution.

Negatively charged hydroxide ions are attracted towards the positively charged anode where they are oxidised to molecular oxygen and water:

 $4OH^{-}(aq) \rightarrow O_{2}(g) + 2H_{2}O(l) + 4e^{-}$



b) At the *cathode* (-ve):

Positively charged sodium ions and hydrogen ions (cations) are both attracted to the negative cathode.

Sodium is above hydrogen in the electrochemical series, therefore hydrogen ions are preferentially reduced to molecular hydrogen at the cathode:

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



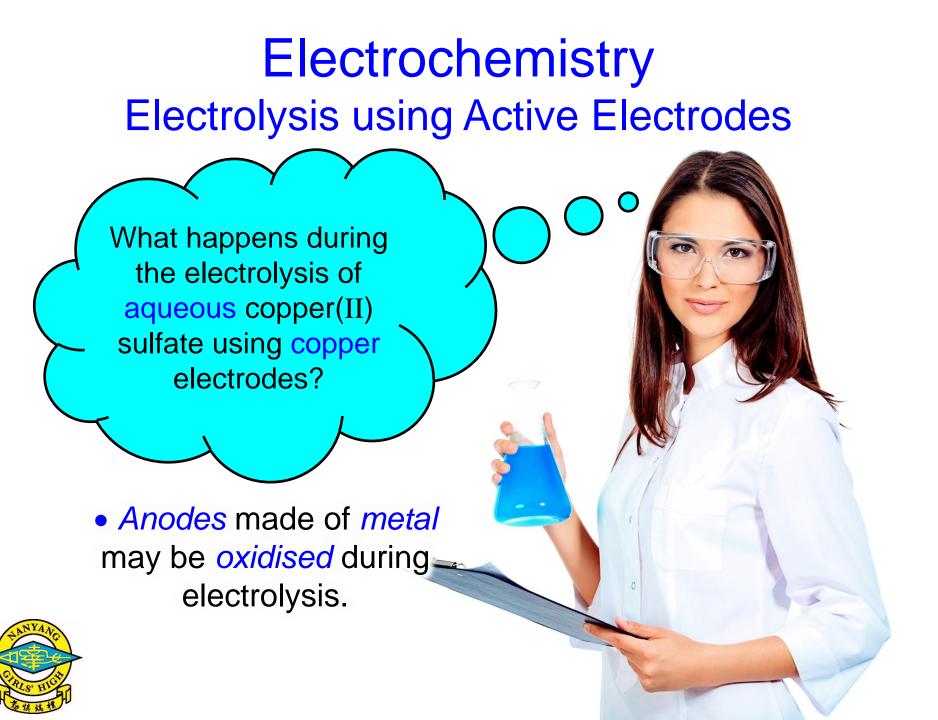
Electrochemistry Electrolysis of Aqueous Electrolytes At the Cathode: More positive / less negative E^{\ominus} is preferentially reduced. Na⁺ + e⁻ \rightleftharpoons Na $E^{\ominus} = -2.71$ V $2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^- E^{\ominus} = -0.83$ V $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

At the Anode

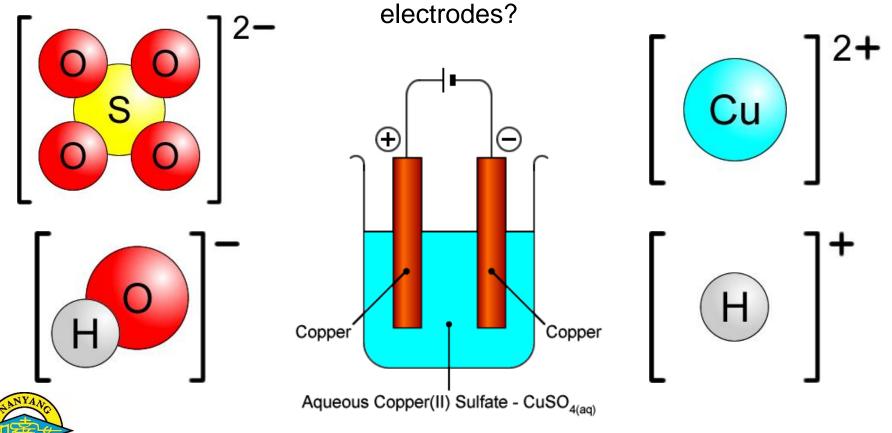
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 What products are formed at a) the anode and b) the cathode when aqueous copper(II) sulfate is electrolysed using copper

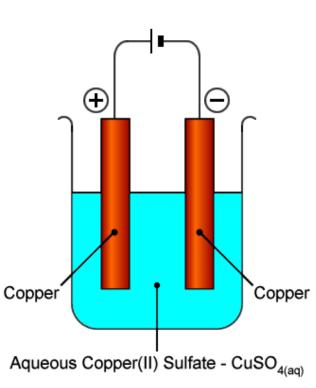


 What products are formed at a) the anode and b) the cathode when aqueous copper(II) sulfate is electrolysed using copper

electrodes?

a) At the anode (+ve):

If the anode is made of a metal whose cations also exist in the electrolyte, then the anode is described as being active, *i.e.* it will participate in the electrolysis and undergo oxidation. In this example, the copper atoms of the anode will be oxidised to form copper(II) ions: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$



b) At the *cathode (-ve)*:

Positively charged copper(II) ions and hydrogen ions (cations) are both attracted to the negative cathode.

Copper is below hydrogen in the electrochemical series, therefore copper(II) ions are preferentially reduced to copper atoms at the cathode:

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

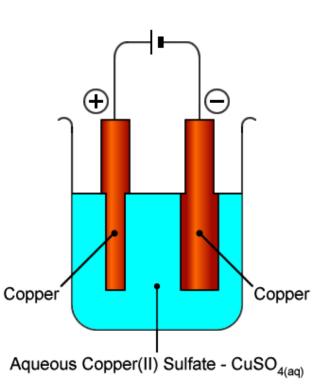


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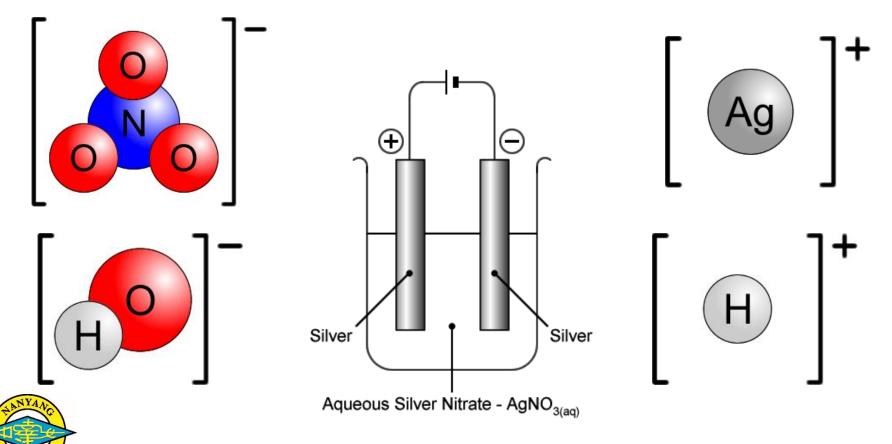
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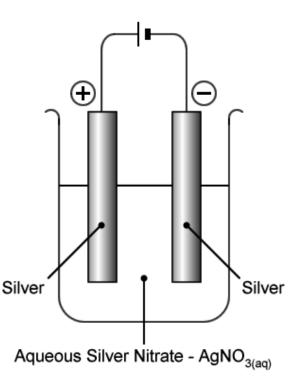
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a) At the anode (+ve):

If the anode is made of a metal whose cations also exist in the electrolyte, then the anode is described as being active, *i.e.* it will participate in the electrolysis and undergo oxidation. In this example, the silver atoms of the anode will be oxidised to form silver ions: $Ag(s) \rightarrow Ag^{+}(aq) + e^{-}$



b) At the *cathode* (-ve):

Positively charged silver ions and hydrogen ions (cations) are both attracted to the negative cathode.

Silver is below hydrogen in the electrochemical series, therefore silver ions are preferentially reduced to silver atoms at the cathode:

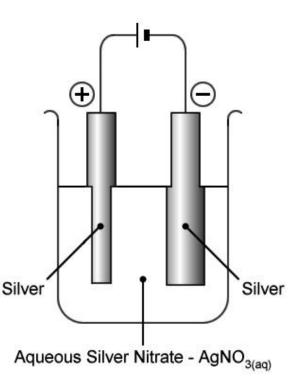
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Electrochemistry Electrolysis using Active Electrodes At the Cathode:

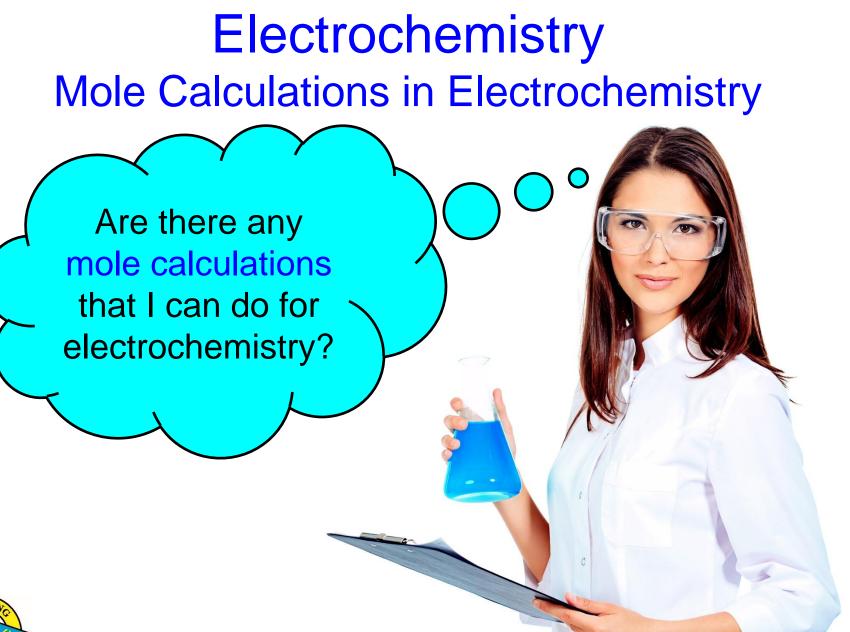
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At the Anode

More negative / less positive E^{\ominus} is preferentially oxidised. More concentrated is preferentially oxidised. $O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \qquad E^{\ominus} = +1.23 \text{ V}$ $Ag^+ + e^- \rightleftharpoons Ag \qquad E^{\ominus} = +0.80 \text{ V}$ $Ag \rightarrow Ag^+ + e^-$



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 The number of moles of electrons that flow through a circuit is given by Faraday's equation of electrolysis:

moles of	current (A) × time (s)
electrons =	96 500

Where...

current = the electrical current that flows through the circuit measured in amperes (amps, A).

time = the time that the electrical current flows for measured in seconds (s).



96 500 = Faraday's Constant measured in coulombs per mole (C mol⁻¹).

 Calculate the mass of pure copper deposited at the cathode during the electrolysis of aqueous coper(II) sulfate if a current of 3.00 A flows for 482.5 minutes.



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a) Convert time into seconds:

482.5 minutes = 482.5 × 60 = 28950 s

b) Calculate moles of electrons that flowed through the circuit in this time:

moles of electrons = $(3.00 \times 28950) \div 96500 = 0.900$ mol



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c) Calculate moles of pure copper deposited:

from the ionic half-equation for reduction of Cu²⁺ at the cathode, $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ 2 mol of electrons deposit 1 mol of Cu(s) $\therefore 0.900$ mol of electrons deposit $\frac{1}{2} \times 0.900 = 0.450$ mol of Cu(s)



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d) Calculate mass of pure copper deposited:

mass in grams = mol × A_r = 0.450 × 63.5 = 28.575 g = <u>28.6 g</u> to 3 s.f.



 The electrolysis of molten sodium chloride produces sodium and chlorine. Calculate the time in seconds taken for a current of 50.0 A to produce 120 dm³ of chlorine gas.



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moles of gas = volume in $dm^3 \div 24.0 = 120 \div 24.0 = 5.00$ mol



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moles of gas = volume in $dm^3 \div 24.0 = 120 \div 24.0 = 5.00$ mol

b) Calculate moles of electrons produced when this many moles of chlorine gas are produced:

from the ionic half-equation for oxidation of Cl^- at the anode, $2Cl(l) \rightarrow Cl_2(g) + 2e^ \therefore$ the production of 1 mol of Cl(g) produces 2 mol of electrons \therefore the production of 5.00 mol of $Cl_2(g)$ produces 2 × 5.00 = 10.0 mol of electrons

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c) Rearrange Faraday's equation of electrolysis... moles of electrons = (current in A \times time in s) \div 96 500 ...to make *time* the subject of the equation.



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d) Substitute known values into the rearranged version of Faraday's equation and hence calculate the time taken.



time in s = $(10.0 \times 96500) \div 50.0 = 19300$ s

Electrochemistry

Presentation on The Electrolysis of Aqueous Salts, Acids and Alkalis by Dr. Chris Slatter christopher_john_slatter@nygh.edu.sg

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