

VCE Chemistry $\frac{3}{4}$ Features of Electrolytic Cells [2.2] Workbook

Outline:



Non-Standard Conditions

Pg 2-21

- Higher Concentrations
- Molten Conditions

Features of Electrolytic Cells

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- Commercial Cell - Down's Cell
- Molten Electrolyte
- Material of Electrode
- Other Electrolytes Added
- Barrier Within Cell
- Constantly Removing Products
- Enclosed Container

Safety and Storage of Hydrogen Gas

Pg 39-43

- Safety of Hydrogen Gas
- Storage of Hydrogen Gas

Production of Hydrogen Gas

Pg 44-61

- Production of Hydrogen Gas
- Polymer Electrolyte Membrane (PEM) Electrolyser
- Artificial Photosynthesis

Learning Objectives:

- ❑ CH34 [2.2.1] - Find electrolytic reactions in non-standard conditions (molten & high concentration)
- ❑ CH34 [2.2.2] - Identify features of electrolytic cells & their purpose
- ❑ CH34 [2.2.3] - Identify key features, write reactions & relate to sustainability & green chemistry principles regarding production of green hydrogen (PEM & Artificial Photosynthesis)



Section A: Non-Standard Conditions

Sometimes, we will be given cells which are not at standard conditions.

Discussion: What conditions is the electrochemical series constructed at?

➤ _____.

➤ _____.

Context

➤ Electrolytic cells may be at **different** conditions.

➤ **Result:** Order of the electrochemical series can _____.

Let's first look at what happens at higher concentrations!

Space for Personal Notes

Sub-Section: Higher Concentrations



First, let's have a look at a scenario at standard conditions!



Exploration: Electrolysis Scenario #1



➤ Scenario: Electrolysis of **NaCl(aq)** at SLC and **1.0 M** concentration.

➤ Where is everything on the ECS? (*Label Below*)

Reaction	Standard Electrode Potential (E°) In Volts At 25°C
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2e^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	+1.77
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6e^- \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$	+1.36
$\text{Cl}_2(\text{g}) + 2e^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$	+1.36
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4e^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	+1.23
$\text{Br}_2(\text{l}) + 2e^- \rightleftharpoons 2\text{Br}^-(\text{aq})$	+1.09
$\text{Zn}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Zn}(\text{s})$	-0.76
$2\text{H}_2\text{O}(\text{l}) + 2e^- \rightleftharpoons \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Mn}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Mn}(\text{s})$	-1.18
$\text{Al}^{3+}(\text{aq}) + 3e^- \rightleftharpoons \text{Al}(\text{s})$	-1.66
$\text{Mg}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Mg}(\text{s})$	-2.37
$\text{Na}^+(\text{aq}) + e^- \rightleftharpoons \text{Na}(\text{s})$	-2.71
$\text{Ca}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Ca}(\text{s})$	-2.87

► Reactions Which Occur:

Strongest Oxidant: _____	Strongest Reductant: _____
Cathode (Reduction) Half-Equation:	Anode (Oxidation) Half-Equation:

Discussion: Relative Oxidant/Reductant Strength



<u>Reaction</u>	<u>Standard Electrode Potential (E°) In Volts At 25°C</u>
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2e^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	+1.77
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6e^- \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$	+1.36
$\text{Cl}_2(\text{g}) + 2e^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$	+1.36
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4e^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	+1.23
$\text{Br}_2(\text{l}) + 2e^- \rightleftharpoons 2\text{Br}^-(\text{aq})$	+1.09
$\text{Zn}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Zn}(\text{s})$	-0.76
$2\text{H}_2\text{O}(\text{l}) + 2e^- \rightleftharpoons \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Mn}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Mn}(\text{s})$	-1.18
$\text{Al}^{3+}(\text{aq}) + 3e^- \rightleftharpoons \text{Al}(\text{s})$	-1.66
$\text{Mg}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Mg}(\text{s})$	-2.37
$\text{Na}^+(\text{aq}) + e^- \rightleftharpoons \text{Na}(\text{s})$	-2.71
$\text{Ca}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Ca}(\text{s})$	-2.87

➤ Comparing **relative oxidant/reductant strength** of substances:

⚙ **Relative reductant strength** of chloride compared to water: [close] / [far] in strength

⚙ **Relative oxidant strength** of sodium ions compared to water: [close] / [far] in strength

Consider the following analogy!

Analogy: Pushing in Line to Reach the Finish I

➤ **Scenario #1:** Imagine two people trying to push into line.

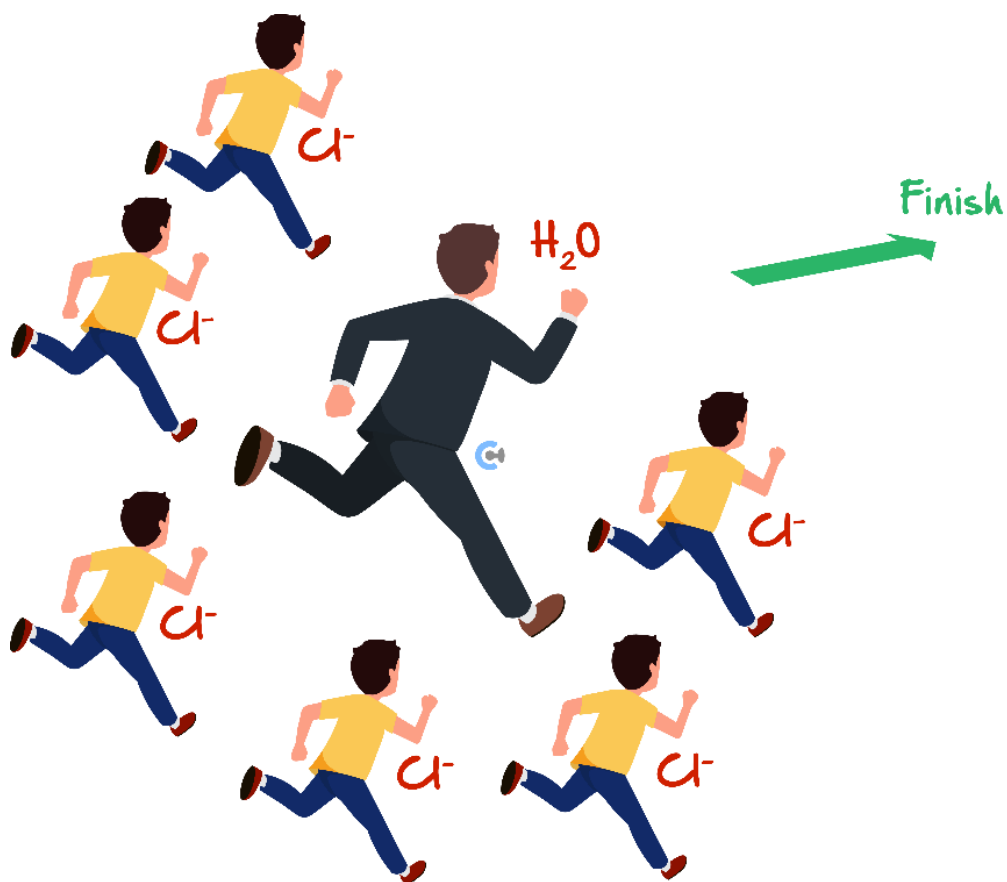
$\text{H}_2\text{O}(\text{l})$	$\text{Cl}^-(\text{aq})$
Huge Strong Person	Little Kid



➤ Who will win?

[Strong Person (H_2O)] / [Weaker Kid (Cl^-)]

➤ Scenario #2: Cl^- is in higher concentration.



➤ Who will win now?

[Strong Person (H_2O)] / [Weaker Kids (Cl^-)]

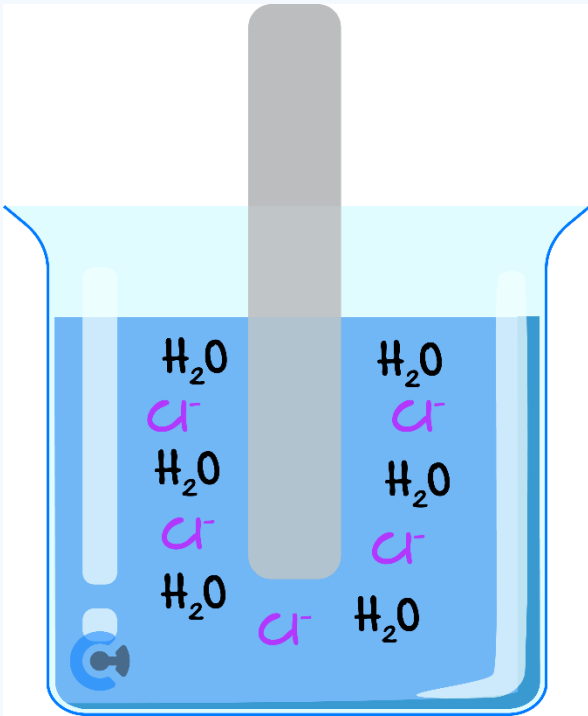
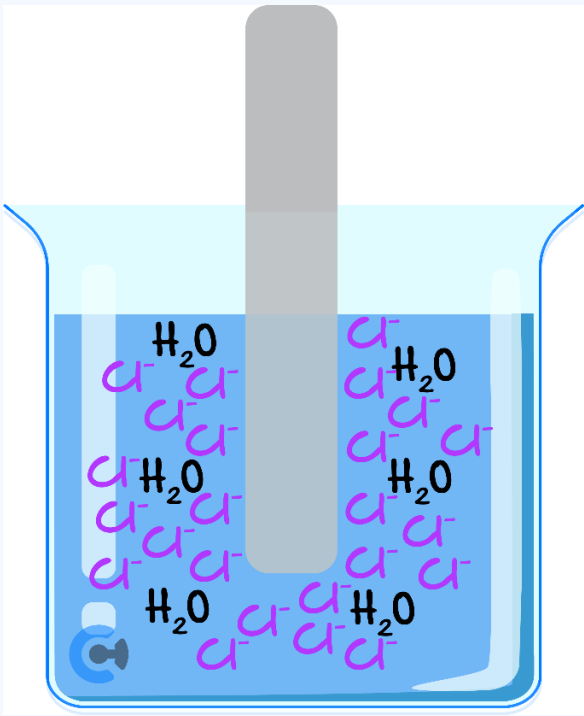
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Let's link that to actual electrolysis now!



Exploration: 1.0 M vs 5.0 M Concentration

➤ Water & chloride at different concentrations:

1.0 M Concentration	5.0 M Concentration
	
<p>➤ Water _____ reacts as it is stronger.</p>	<p>➤ Even though water is stronger, there is more chloride (Cl^-)!</p> <p>➤ The chloride _____ the water and reacts in preference!</p>

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How about Na^+ ?

Analogy: Pushing in Line to Reach the Finish II

➤ Scenario #1: Imagine two people trying to push into line.

$\text{H}_2\text{O}(\text{l})$	$\text{Na}^+(\text{aq})$
Huge Strong Person	Ant



➤ Who will win?

$[\text{Strong Person } (\text{H}_2\text{O})] / [\text{Ant } (\text{Na}^+)]$

➤ Scenario #2: Na^+ is in higher concentration.



➤ Who will win now?

$[\text{Strong Person } (\text{H}_2\text{O})] / [\text{Ants } (\text{Na}^+)]$

Let's link that to actual electrolysis now!



Exploration: Sodium Ions (Na^+) at 5.0 M Concentration

➤ Water & sodium ions at different concentrations:

1.0 M Concentration	5.0 M Concentration
<p>➤ Water _____ reacts as it is stronger.</p>	<p>➤ Even though there are more sodium ions (Na^+), water is significantly stronger!</p> <p>➤ Water still _____ to sodium ions!</p>

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Let's have a look at this on the electrochemical series!



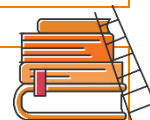
Exploration: Electrolysis of NaCl at Higher Concentrations

- Where are the relevant species on the electrochemical series? *(Label Below)*
- What is the strongest reductant now? What is the strongest oxidant now? *(Label Below)*

<u>Reaction</u>	<u>Standard Electrode Potential (E°) In Volts At 25°C</u>
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2e^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	+1.77
$\text{Au}^+(\text{aq}) + e^- \rightleftharpoons \text{Au}(\text{s})$	+1.68
$\text{Cl}_2(\text{g}) + 2e^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$	+1.36
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4e^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	+1.23
$\text{Br}_2(\text{l}) + 2e^- \rightleftharpoons 2\text{Br}^-(\text{aq})$	+1.09
$\text{Ag}^+(\text{aq}) + e^- \rightleftharpoons \text{Ag}(\text{s})$	+0.80
$\text{Fe}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Fe}(\text{s})$	-0.44
$\text{Zn}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Zn}(\text{s})$	-0.76
$2\text{H}_2\text{O}(\text{l}) + 2e^- \rightleftharpoons \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Mn}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Mn}(\text{s})$	-1.18
$\text{Al}^{3+}(\text{aq}) + 3e^- \rightleftharpoons \text{Al}(\text{s})$	-1.66
$\text{Mg}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Mg}(\text{s})$	-2.37
$\text{Na}^+(\text{aq}) + e^- \rightleftharpoons \text{Na}(\text{s})$	-2.71
$\text{Ca}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Ca}(\text{s})$	-2.87

<u>Cathode (Reduction) Half-Reaction</u>	<u>Anode (Oxidation) Half-Reaction</u>

Extension: How much do each of the oxidants/reductants increase in strength by at higher concentrations?



➤ Consider sodium ions (Na^+) and water (H_2O) vs chloride (Cl) and water (H_2O):

<u>Reaction</u>	<u>Standard Electrode Potential (E°) In Volts At 25°C</u>
$\text{Cl}_2(\text{g}) + 2e^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$	+1.36
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4e^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	+1.23
$2\text{H}_2\text{O}(\text{l}) + 2e^- \rightleftharpoons \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Mn}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Mn}(\text{s})$	-1.18
$\text{Al}^{3+}(\text{aq}) + 3e^- \rightleftharpoons \text{Al}(\text{s})$	-1.66
$\text{Mg}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Mg}(\text{s})$	-2.37
$\text{Na}^+(\text{aq}) + e^- \rightleftharpoons \text{Na}(\text{s})$	-2.71

➤ What is the difference in EMF between:

<u>Chloride (Cl) And Water (H_2O)</u>	<u>Sodium Ions (Na^+) And Water (H_2O)</u>

Space for Personal Notes



Electrolysis of NaCl at Higher Concentrations

Conditions	Sodium ions (Na^+)	Chloride (Cl^-)
1.0 M Concentration	[slightly] / [significantly] weaker oxidant than water	[slightly] / [significantly] weaker reductant than water
4.0 M Concentration	[will] / [will not] reduce in preference to water	[will] / [will not] oxidise in preference to water

- Cutoff for "High Concentration": _____.
- **Note:** Only _____ at high concentration is mainly tested!
- **Additional Information:** As $\text{Cl}^-(\text{aq})$ is very close in reductant strength to water at most concentrations (1.0 M – 5.0 M), _____ chloride and water are oxidising **simultaneously!**

Your turn!



Question 1

The electrolysis of 5.0 M concentration of calcium chloride ($\text{CaCl}_2(\text{aq})$) is undertaken with inert electrodes.

Write the half-equations which occur at the:

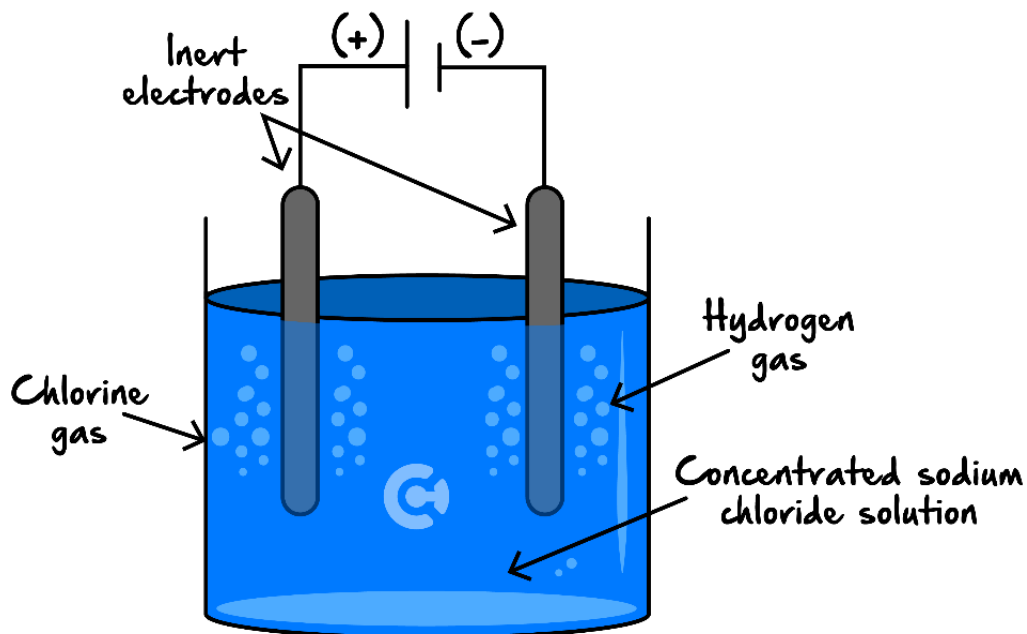
- a. Positive electrode.

- b. Negative electrode.

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Question 2

A concentrated sodium chloride solution is electrolysed. The process can be simply represented by the following diagram:



During the electrolysis of this electrolyte:

- A. The rate of reaction would increase.
- B. The pH of the solution would decrease.
- C. The pH of the solution would increase.
- D. The gas formed at the negative electrode would be different.

Question 3 Additional Question.

In the electrolysis of an aqueous solution of NaCl, which species is most likely to be reduced at the cathode?

- A. Na^+ ions
- B. Water molecules
- C. Cl^- ions
- D. O_2 molecules

Question 4 Additional Question.

How does the concentration of halide ions typically affect the reaction at the anode in aqueous electrolysis?

- A. High concentrations always cause halide ions to oxidise in preference to water.
- B. Under typical (dilute) conditions, water is oxidised rather than halide ions.
- C. Low concentrations favour the oxidation of halide ions.
- D. The concentration of halide ions has no effect on the anodic reaction.

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Sub-Section: Molten Conditions



Now, let's have a look at cells in molten conditions!



Discussion: What Are Molten Conditions?



Molten



➤ **Definition:** The liquid form of solid extremely hazardous substance at _____ temperatures, which is normally in solid form at SLC conditions.

Discussion: Is water present in molten conditions?



[Yes] / [No] / [Maybe]

Space for Personal Notes



Context

- In the previous section, can sodium ions react even at higher concentrations? [Yes] / [No]
- What reacts in preference? _____
- In molten conditions, is this water present? [Yes] / [No]
- **Conclusion:** Molten Conditions are used to react everything which is weaker than water!

<u>Reaction</u>	<u>Standard Electrode Potential (E°) In Volts At 25°C</u>
$\text{Fe}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Fe}(\text{s})$	-0.44
$\text{Zn}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Zn}(\text{s})$	-0.76
$2\text{H}_2\text{O}(\text{l}) + 2e^- \rightleftharpoons \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Mn}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Mn}(\text{s})$	-1.18
$\text{Al}^{3+}(\text{aq}) + 3e^- \rightleftharpoons \text{Al}(\text{s})$	-1.66
$\text{Mg}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Mg}(\text{s})$	-2.37
$\text{Na}^+(\text{aq}) + e^- \rightleftharpoons \text{Na}(\text{s})$	-2.71
$\text{Ca}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Ca}(\text{s})$	-2.87
$\text{K}^+(\text{aq}) + e^- \rightleftharpoons \text{K}(\text{s})$	-2.93
$\text{Li}^+(\text{aq}) + e^- \rightleftharpoons \text{Li}(\text{s})$	-3.04

Space for Personal Notes

Let's look at a question together!



Question 5 Walkthrough.

Potassium chloride is electrolysed using an iron cathode and a graphite anode at molten conditions.

Write the half-equations which occur at the following electrodes. **Do not include states yet.**

a. Cathode.

b. Anode.

Discussion: What is the state of potassium ions (K^+) at molten conditions?





Non-Standard Condition Reactions



➤ At higher concentrations, chloride ions (Cl^-) react in preference to water.

➤ Molten Conditions:

 Water [is] / [is not] present!

 State of cations/anions are **not aqueous (aq)**, but instead are _____.

Your turn!



Question 6

Molten calcium fluoride (CaF_2) is electrolysed using a cobalt cathode and a graphite anode.

- a. Write the half-equation for the reduction reaction.

- b. Write the half-equation for the oxidation reaction.

Question 7

A molten mixture of manganese fluoride is electrolysed.

- a. Write the half-equation for the reduction reaction.

- b. Write the half-equation for the oxidation reaction.

NOTE: Although there's the following equation, the Mn^{2+} requires liquid water in order to oxidise!



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Try some more questions!



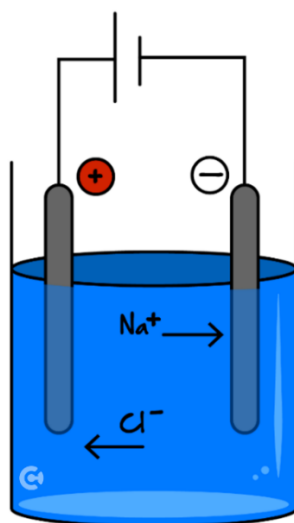
Question 8

A molten mixture of equal parts aluminum fluoride, AlF_3 , and sodium chloride, NaCl , undergoes electrolysis. Which one of the following statements about this reaction is correct?

- A. Sodium metal will be produced at the cathode and fluorine gas will be produced at the anode.
- B. Sodium metal will be produced at the anode and chlorine gas will be produced at the cathode.
- C. Aluminum metal will be produced at the cathode and chlorine gas will be produced at the anode.
- D. Aluminum metal will be produced at the anode and fluorine gas will be produced at the cathode.

The following information applies to the two questions that follow:

An electrolytic cell uses inert electrodes placed in a solution of NaCl .



Question 9

If the solution is a molten one:

- A. Sodium metal will form at the cathode and chlorine gas at the anode.
- B. Sodium metal will form at the anode and chlorine gas at the cathode.
- C. Hydrogen gas will form at the anode and oxygen gas at the cathode.
- D. Hydrogen gas will form at the cathode and chlorine gas at the anode.

Question 10

If the solution is a concentrated aqueous one:

- A. Hydrogen gas will form at the cathode and oxygen at the anode.
- B. Sodium will form at the cathode and oxygen at the anode.
- C. Hydrogen gas will form at the anode and oxygen gas at the cathode.
- D. Hydrogen gas will form at the cathode and chlorine gas at the anode.

Try a really hard VCAA Question!


Question 11 (3 marks)


Inspired from VCAA Chemistry Exam 2021

<https://www.vcaa.vic.edu.au/Documents/exams/chemistry/2021/2021chem-w.pdf#page=19>

Potassium ions can be obtained from potassium chloride, KCl, which can be obtained from seawater.

Explain how K can be produced from KCl in an electrolytic cell.

Question 12 Additional Question.

An electrolysis cell is set up with inert platinum, Pt, electrodes.

Which one of the following will produce a gas at the cathode when undergoing electrolysis in the cell?

- A. Potassium iodide, KI(aq).
- B. Sodium chloride, NaCl(l).
- C. Lead bromide, PbBr₂(l).
- D. Copper sulphate, CuSO₄(aq).

Space for Personal Notes

Section B: Features of Electrolytic Cells

Sub-Section: Commercial Cell – Down's Cell



Now that we've looked at how to predict the reactions which occur, let's have a look at some electrolytic cells in real life!



Discussion: Will sodium generally exist in its ion form (Na^+) or metal form (Na) in nature when it is mined from the ground?



Discussion: Sodium will generally exist in its ion form. What if the pure metal form of a metal such as sodium (Na) wants to be obtained? What needs to be done?



Context

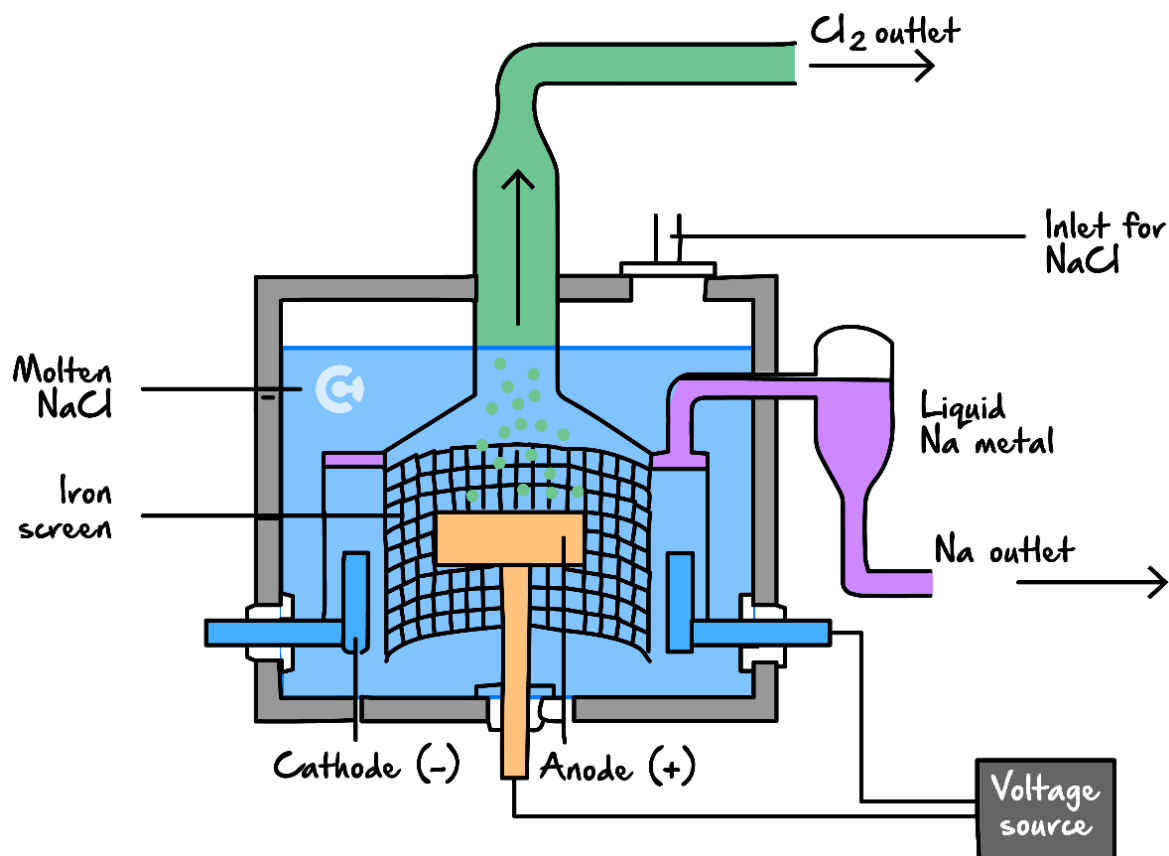


- **Electrolysis Purpose:** Produces products unlikely to exist in nature.
- **Example:** Down's Cell is used to produce pure sodium metal.
- **Relevance:** While not explicitly in the study design, understanding its construct is useful as commercial **cell features are tested**.

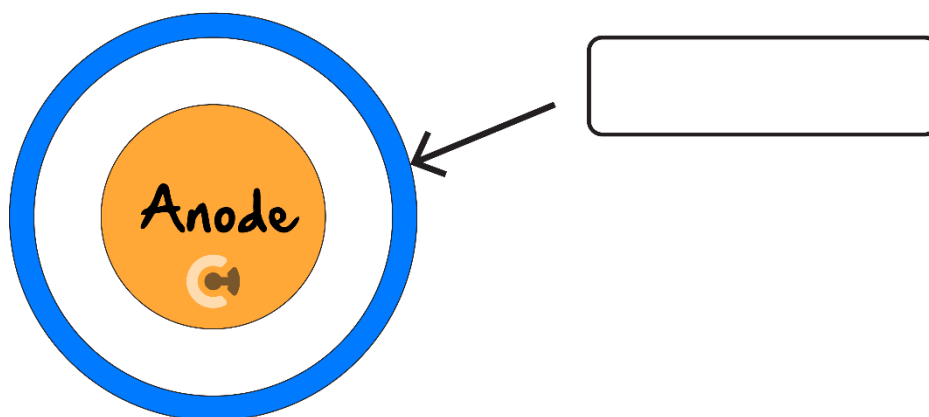
Let's look at Down's Cell Together!

Exploration: Down's Cell

- Down's cell aims to turn sodium ions (Na^+) into sodium metal (Na).



Top View



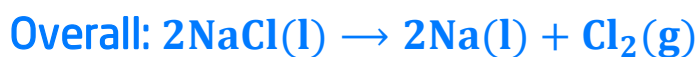
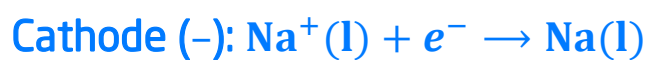
- In Down's Cell, a **molten sodium chloride** (NaCl(l)) electrolyte is electrolysed.

➤ Equations:

Cathode (Reduction) Half-Reaction	Anode (Oxidation) Half-Reaction

🔄 Overall Reaction: _____

➤ Equations:



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Sub-Section: Molten Electrolyte

REMINDER: This cell aims to produce sodium metal.

Discussion: Why is molten NaCl used? What's wrong with aqueous or concentrated NaCl (brine)?

<u>Conditions</u>	<u>Cathode Reaction</u>	<u>Anode Reaction</u>
1.0 M NaCl	$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2(\text{g})$	$\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g})$
4.0 M NaCl	$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2(\text{g})$	$\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g})$
Molten NaCl	$\text{Na}^+(\text{l}) \rightarrow \text{Na}(\text{s})$	$\text{Cl}^-(\text{l}) \rightarrow \text{Cl}_2(\text{g})$

➤ Reason for Using Molten NaCl: _____.

Molten Electrolyte Purpose

➤ To react with species weaker than water.

Space for Personal Notes



Sub-Section: Material of Electrode



Exploration: Electrode Material

➤ In Down's Cell:

<u>Anode Material</u>	<u>Cathode Material</u>

➤ Scenario #1: Platinum is both inert & catalytic. Why isn't it used instead?

➤ Scenario #2: Why can iron be used at the cathode? Won't it react in preference to chloride (Cl^-)?

<u>Reaction</u>	<u>Standard Electrode Potential (E°) In Volts At 25°C</u>
$\text{Cl}_2(\text{g}) + 2e^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$	+1.36
$\text{Br}_2(\text{l}) + 2e^- \rightleftharpoons 2\text{Br}^-(\text{aq})$	+1.09
$\text{Co}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Co}(\text{s})$	-0.28
$\text{Fe}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Fe}(\text{s})$	-0.44

⚙ Reasoning: _____.

⚙ Question: Why do we use iron used instead of graphite at the cathode?



Electrode Material

➤ Platinum Electrodes not used: _____.

➤ Iron used at cathode: _____.

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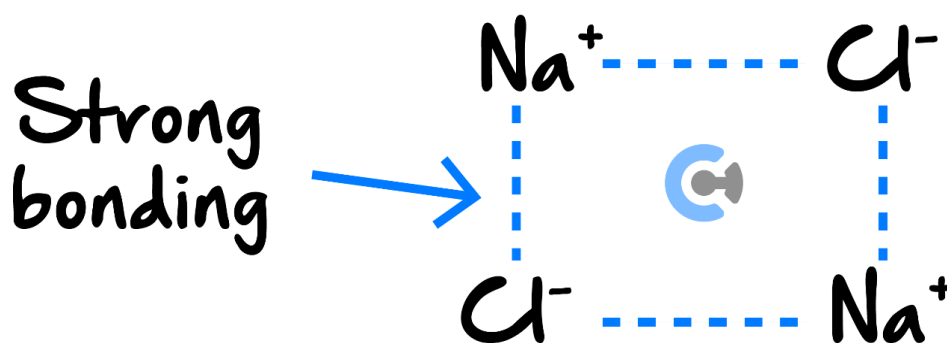
Sub-Section: Other Electrolytes Added

Exploration: Electrolyte

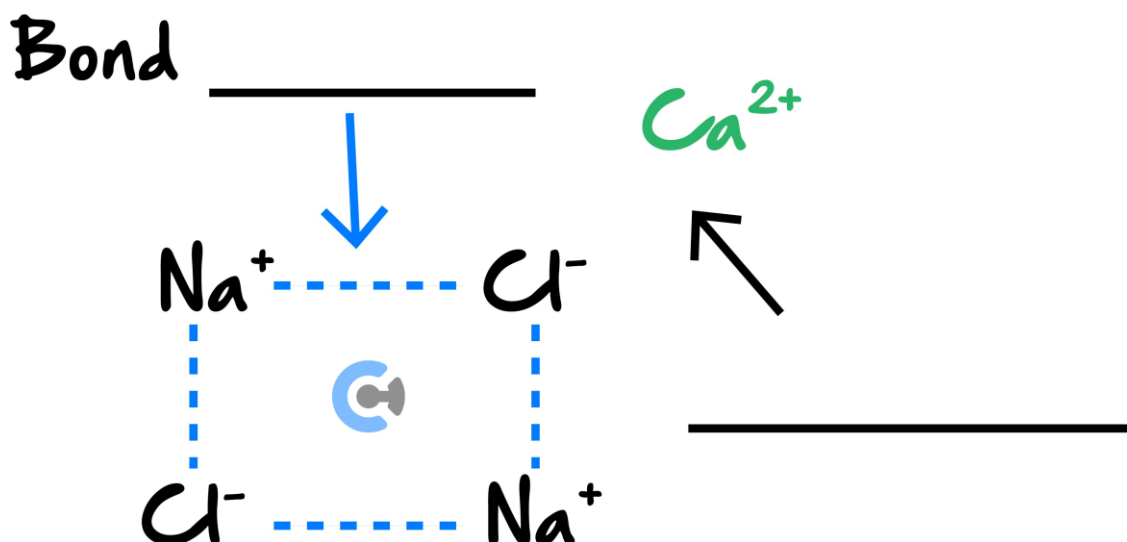
- Electrolyte of Down's Cell is comprised of both molten NaCl(l) and $\text{CaCl}_2(\text{l})$.
- Melting point of pure molten NaCl (l) : _____.

Why do we add Ca^{2+} ions?

- NaCl ionic lattice:



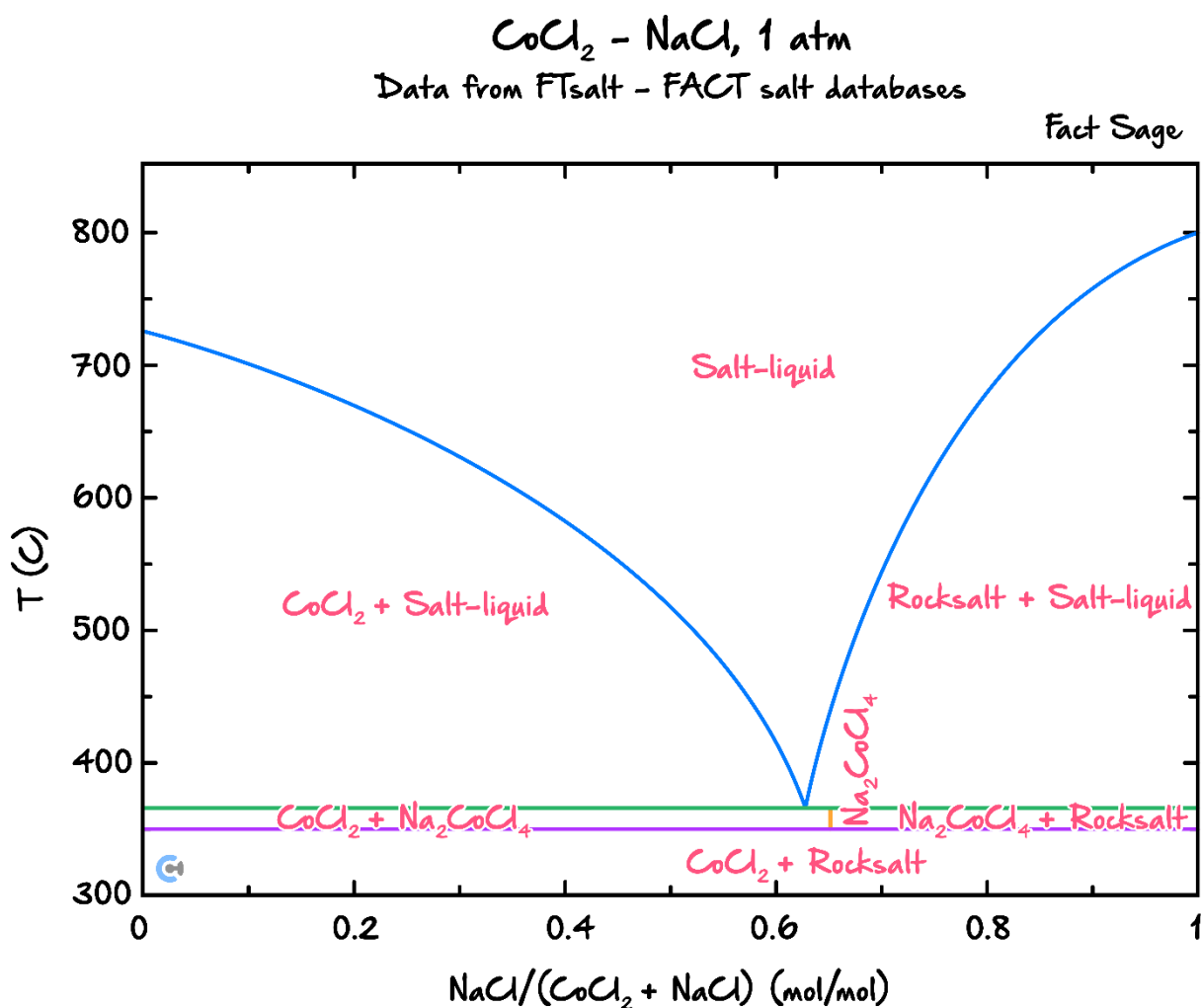
- NaCl ionic lattice with Ca^{2+} ions are added:



- **Effect:** Ca^{2+} ions forms bonds with the Cl^- , effectively _____ the ionic bond between the Na^+ and Cl^- .
- **Result:** This lowers the melting point of the molten NaCl (l) to roughly _____.



Extension: How does adding another ion like calcium ions (Ca^{2+}) lower the overall melting point? (Completely outside the study design (University Chemistry))



- **Effect of Ca^{2+} addition:** Weakens NaCl ionic bonding, lowering melting point.
- **Colligative property:** NaCl dissolves in molten CaCl_2 , reducing melting point.
- **Entropy increase:** Ca^{2+} disperses particles, increasing randomness.

Discussion: What are the benefits of lowering the overall melting point of the electrolytic cell?



- _____.
- _____.



Exploration: Will $\text{Ca}^{2+}(\text{aq})$ Interfere With The Reaction?

<u>Reaction</u>	<u>Standard Electrode Potential (E°) In Volts At 25°C</u>
$\text{Mg}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Mg}(\text{s})$	-2.37
$\text{Na}^+(\text{aq}) + e^- \rightleftharpoons \text{Na}(\text{s})$	-2.71
$\text{Ca}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Ca}(\text{s})$	-2.87
$\text{K}^+(\text{aq}) + e^- \rightleftharpoons \text{K}(\text{s})$	-2.93

[yes] / [no] / [maybe]

- **Reasoning:** Ca^{2+} is _____ on the electrochemical series than Na^+ , and thus, will not reduce in preference.

Adding Other Electrolytes



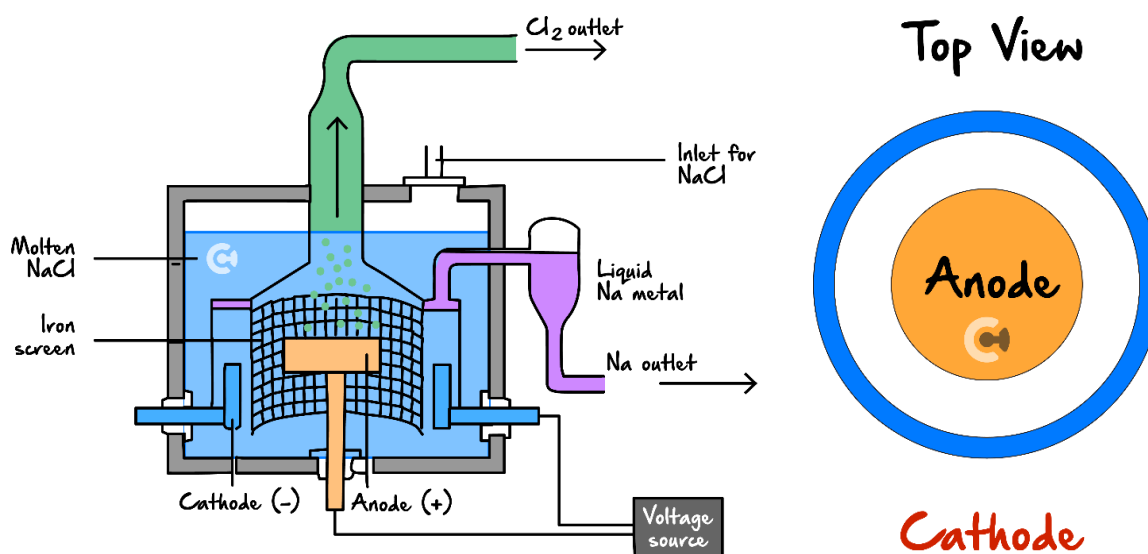
- Other Electrolytes (e.g. CaCl_2) are added to _____.
- **Advantages:** Reduce energy required, cost.

Space for Personal Notes

Sub-Section: Barrier Within Cell

Exploration: Barrier

- Commercial electrolytic cells usually have some **barrier** to **separate the electrodes apart**.
- In Down's Cell, this can be seen from the iron mesh screen, separating the cathode and anode apart.



Why is there a barrier which separates the cathode and anode apart?

- Consider the products which are formed (Cl₂(g) and Na(l)).

Reaction	Standard Electrode Potential (E°) In Volts At 25°C
$\text{Cl}_2(\text{g}) + 2e^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$	+1.36
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4e^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	+1.23 V
$\text{Mg}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Mg}(\text{s})$	-2.37
$\text{Na}^+(\text{aq}) + e^- \rightleftharpoons \text{Na}(\text{s})$	-2.71

<u>Cl₂(g)</u>	<u>Na(l)</u>
[strong] / [weak] oxidant	[strong] / [weak] reductant

- If Cl₂(g) and Na(l) come in direct contact: _____.
- Barrier Purpose: To prevent products from spontaneously re-reacting with each other.
- Scenario: Iron mesh is used instead of a solid iron, which allows some substances to pass through.
 - ⚙ Substances which can pass through: _____.
 - ⚙ Ion passing through purpose:

Barrier Within Electrolytic Cell

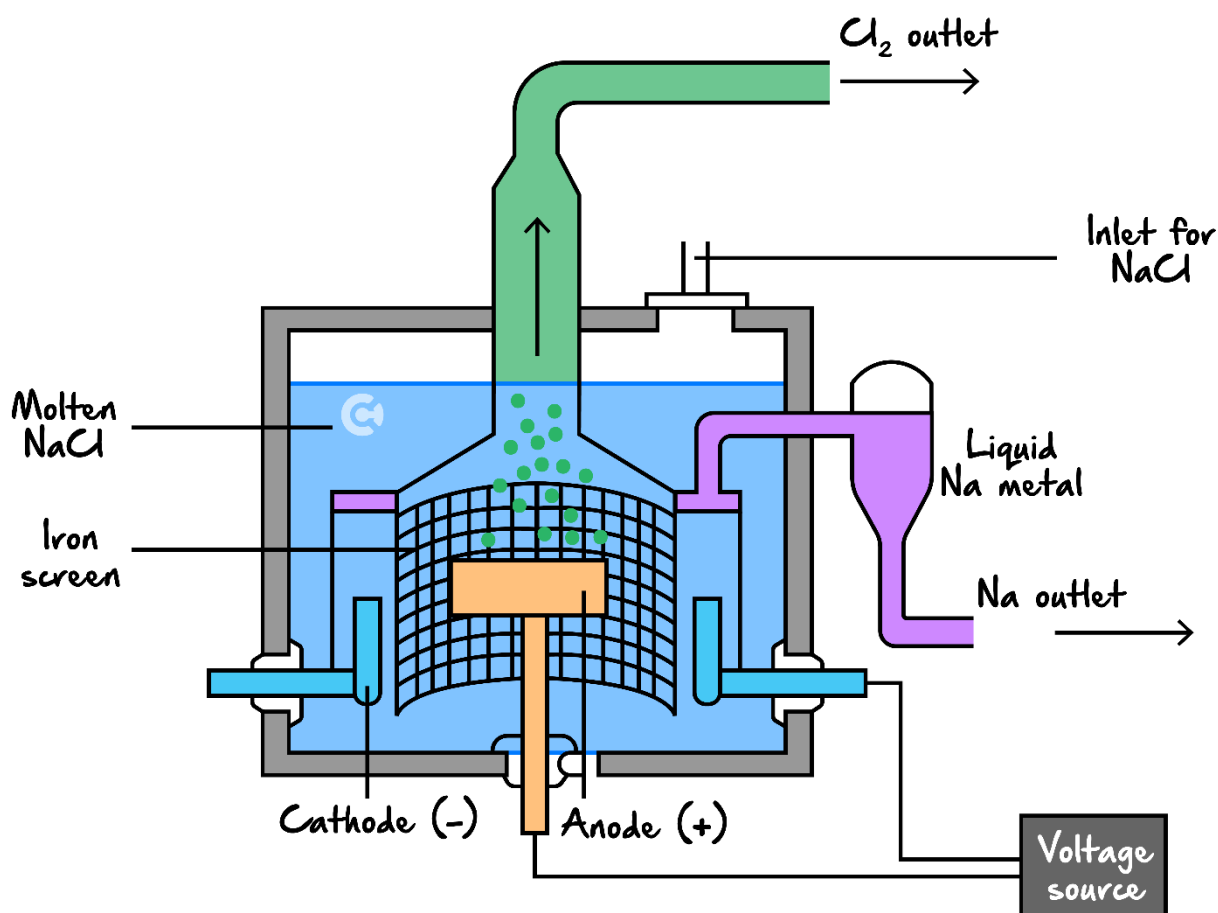


- Purpose:
 - ⚙ To separate products to prevent direct contact and spontaneous redox reaction.
 - ⚙ Allow flow of ions.

Space for Personal Notes

Sub-Section: Constantly Removing Products

Exploration: Products are Removed as Produced



- Sodium liquid metal is less dense than electrolyte.
- What happens when Na metal is produced? *(Label Above)*
- Why is Na constantly funnelled out? _____.

Constantly Removing Products

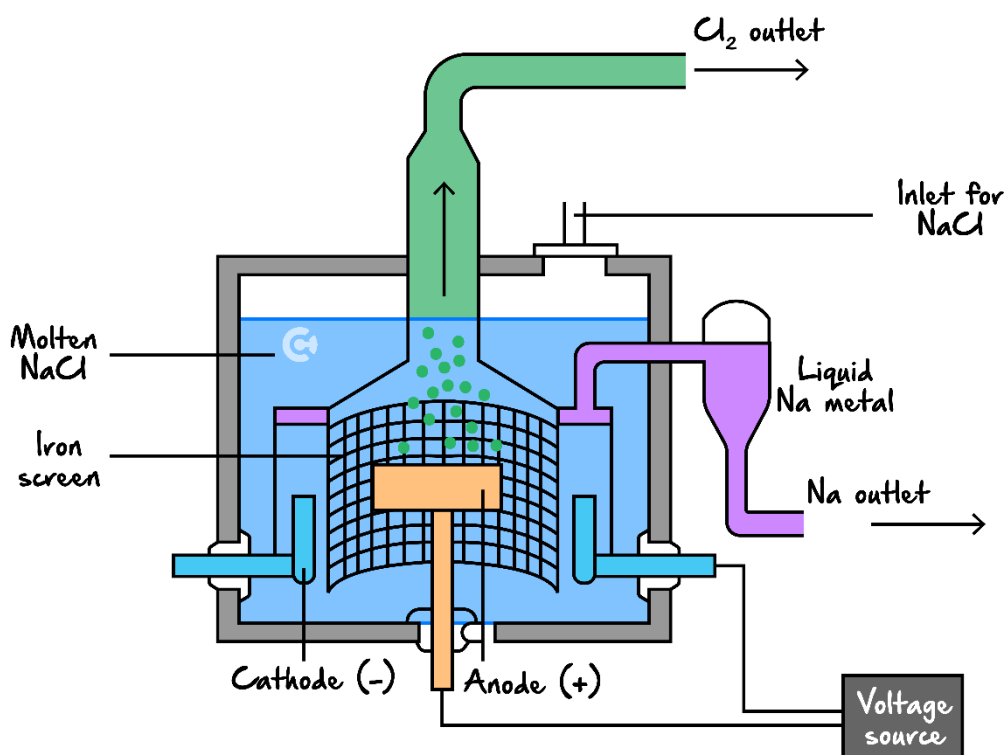
➤ Purpose:

- To reduce chance of products coming _____ with one another and reacting back.
- To prevent _____ products which may _____ with reaction.

Sub-Section: Enclosed Container

Exploration: Enclosed Container

- Commercial electrolytic cells are usually completely enclosed.



- What is present on the outside of the cell? _____
- What happens if it touches the molten sodium (Na(l))? _____

Reaction	Standard Electrode Potential (E°) In Volts At 25°C
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$	+1.36
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	+1.23 V
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Mg}(\text{s})$	-2.37
$\text{Na}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Na}(\text{s})$	-2.71

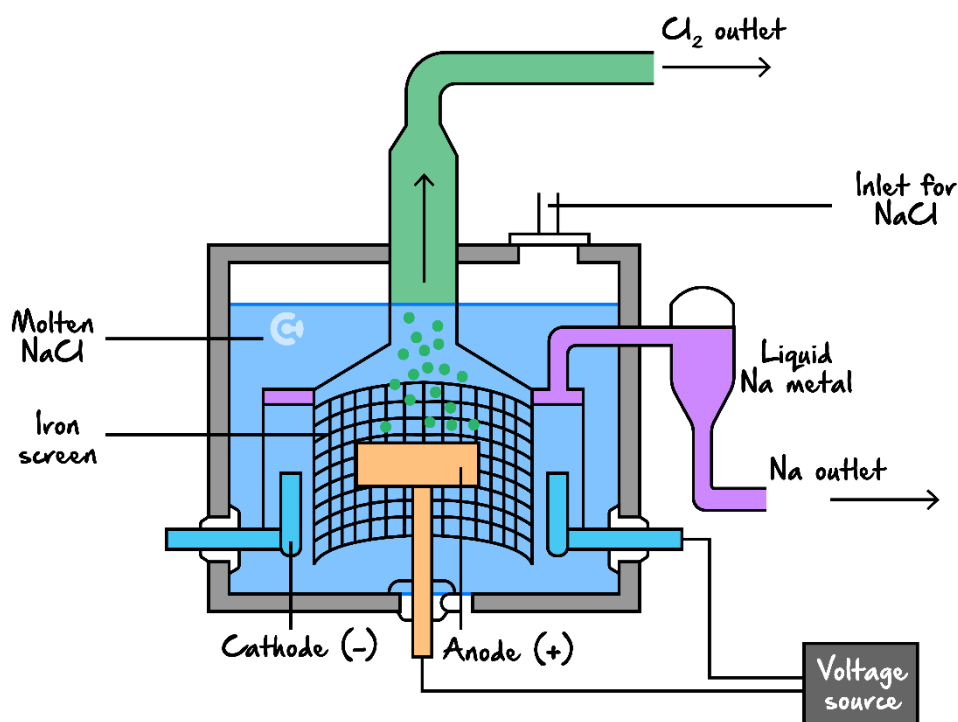
- The container is usually completely enclosed to prevent oxygen gas from spontaneously reacting with the products, which may cause an _____!
- This also results in the products re-reacting back into the reactants!

Enclosed Container

- **Purpose:** To prevent oxygen gas from spontaneously reacting with products.



Features of Electrolytic Cells



- Molten Electrolyte: Reacts with species weaker than water.
- Iron at the cathode: Cathode unreactive - cheaper.
- Other Electrolytes (e.g., CaCl_2) added: Lower melting point of electrolyte.
- Barrier within the cell: Prevent products from spontaneously re-reacting. Still allow flow of ions.
- Products constantly removed: Don't re-react back. No interfere reaction.
- Enclosed container: Prevent O_2 from outside reacting spontaneously.

Try applying these to different cells!



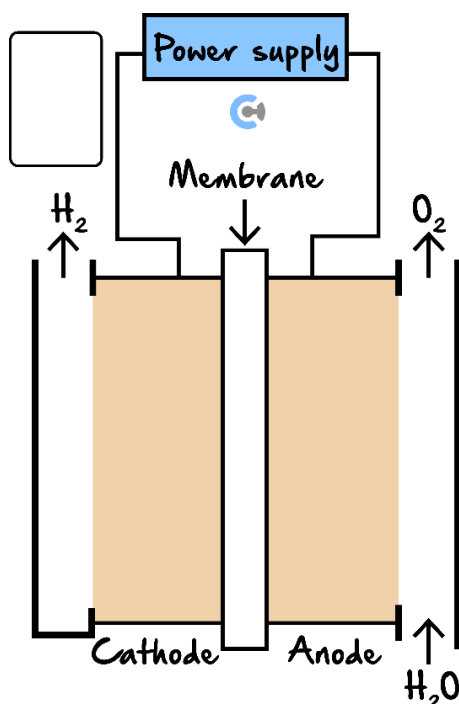
Question 13 (5 marks)



Inspired from VCAA Chemistry Exam 2022

<https://www.vcaa.vic.edu.au/Documents/exams/chemistry/2022/2022chem-w.pdf#page=16>

Hydrogen, H_2 , can be produced using electricity generated by renewable sources. A simplified diagram of an acidic electrolyser used to produce hydrogen is shown below.



- a. Draw an arrow in the box provided on the diagram above to show the direction of the flow of electrons through the wire. Justify your answer. (2 marks)

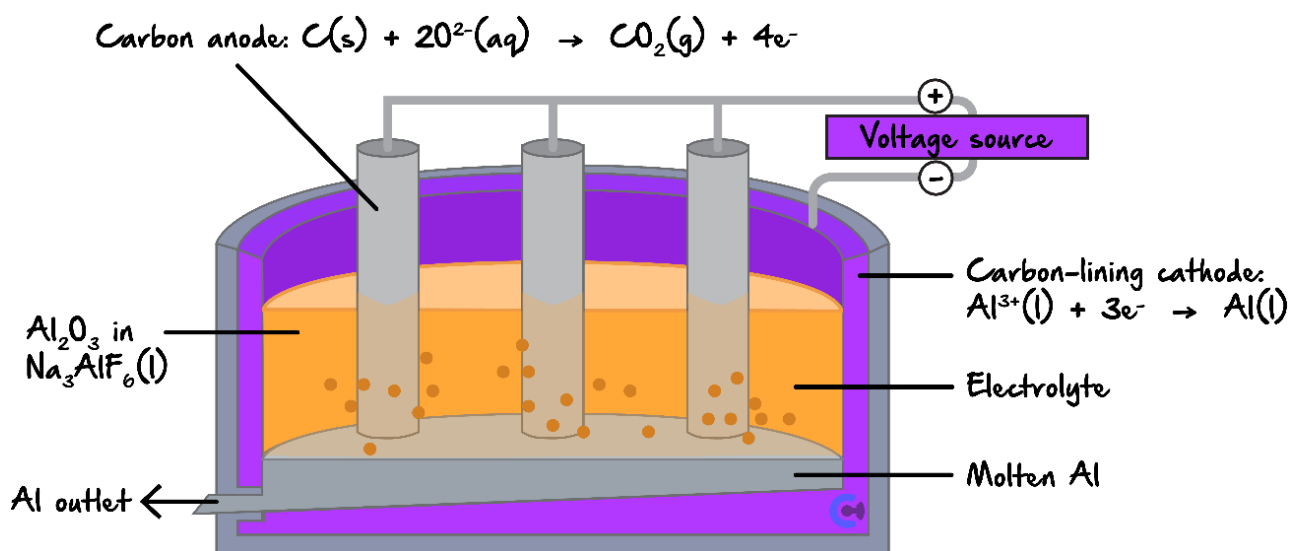
- b. State **two** functions of the membrane. (2 marks)

- c. Write the overall equation for the reaction that takes place in the acidic electrolyser shown in the diagram above when it is operating at 80°C. (1 mark)

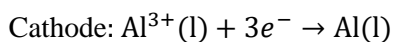
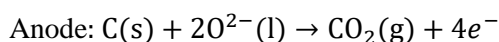
Question 14

The Hall-Heroult cell involves the electrolysis of molten aluminum oxide (Al_2O_3).

A diagram of the cell is provided below:



The reactions which take place are the following:



- a. The liquid aluminum is constantly pumped out of the cell. Provide an explanation for this.

- b. A solution of cryolite (Na_3AlF_6) is also added to this cell. Propose one purpose for the addition of this cryolite. Explain how this helps with the operation of the cell.

Question 15 Additional Question.

In some electrolytic processes, iron is chosen as the cathode material. What is one key reason for using iron at the cathode?

- A. Iron is completely inert and never reacts under electrolytic conditions.
- B. Iron provides a cost-effective, conductive surface that can promote the deposition of the desired product.
- C. Iron significantly raises the cell voltage.
- D. Iron prevents any deposition by repelling cations.

Question 16 Additional Question.

Molten electrolytes are sometimes preferred over aqueous ones in electrolytic cells. Which of the following is a primary reason for this choice?

- A. Water is too expensive compared to molten salts.
- B. Molten electrolytes eliminate competing water-splitting reactions that produce hydrogen and oxygen.
- C. Molten electrolytes inherently produce lower cell voltages.
- D. Aqueous electrolytes have too high conductivity.

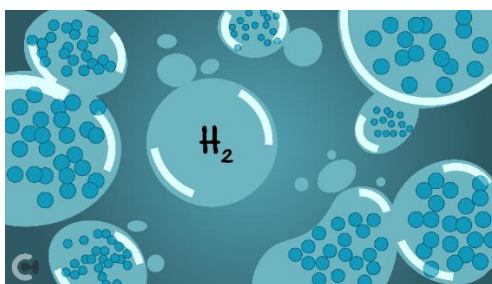
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Section C: Safety and Storage of Hydrogen Gas

Sub-Section: Safety of Hydrogen Gas

Context

- There are issues with safety surrounding hydrogen gas.



- How does hydrogen gas **look** like? _____
- How does hydrogen gas **smell** like? _____
- How does hydrogen gas **taste** like? _____

Why is this an issue?

Exploration: Car Leakage

- Consider two scenarios: One with an oil leak, the other with a hydrogen gas leak.
- How will the hydrogen gas leak look like? *(Draw below)*

Oil leak



Hydrogen gas leak



- Hydrogen gas is _____.

Discussion: How do we know if hydrogen gas is leaking?



Why is hydrogen gas dangerous?



Exploration: Why Else Is Hydrogen Gas Dangerous Then?

- Hydrogen Gas Danger: _____.
- Hydrogen Gas Exploding in Air Video:

<https://youtu.be/nLuOM9a0Wvk?si=0LC2nSIRpo-46RNw&t=45>



Discussion: Why is hydrogen gas being flammable dangerous in a car?



Space for Personal Notes



Discussion: What safety precautions can be taken to help mitigate this risk?

<u>Safety Precaution</u>	<u>Execution</u>
Ignition Protection	
Removal of Combustible Vapours	
Storage Conditions	

Dangers of Hydrogen Gas



- Hydrogen gas is colourless, odourless and tasteless.
 - ⚙ A gas detector is used to detect for its presence.
- Hydrogen gas is highly flammable and explosive.
 - ⚙ Ignition Protection - Keep away from ignition sources.
 - ⚙ Removal of combustible vapours - Use in well ventilated area.
 - ⚙ Storage Conditions - Store in cool and dry areas.
 - ⚙ Physical protection - Wear PPE.

Space for Personal Notes

Try a question!



Question 17

An aqueous solution of 1.0 M magnesium bromide is electrolysed using inert electrodes.

- a. Write the half-equation for the reaction which takes place at the cathode.

- b. The electrolysis of this solution is considered to be dangerous. Explain why it is dangerous, and a safety precaution which can be implemented to help mitigate this risk.

Space for Personal Notes

Sub-Section: Storage of Hydrogen Gas

Exploration: How is hydrogen gas stored?



- Hydrogen gas is stored in a gas tank as a _____.
- Why is hydrogen gas usually stored as a liquid?
 - ⚙ _____.
 - ⚙ _____.
- **Scenario:** Boiling point of hydrogen gas is very low (-250°C).
- **Issue:** Hard to turn it into a liquid.
- **Method to turn $\text{H}_2(\text{g}) \rightarrow \text{Liquid}$ without lowering the temp. to -250°C :** _____
- **Storage Pressure Conditions of $\text{H}_2(\text{g})$:** _____

Storage of Hydrogen Gas

- Hydrogen Gas is stored as liquid under high pressure.
- Reasoning:
 - ⚙ _____.
 - ⚙ _____.

*We've covered the safety and storage of hydrogen gas,
but how is the hydrogen gas actually produced?*

Section D: Production of Hydrogen Gas

Sub-Section: Introduction to Producing Hydrogen Gas





Discussion: How Is Hydrogen Gas Produced?

➤ _____.


➤ _____.

Context

➤ Production of Hydrogen is ranked on a scale:

Color	Grey Hydrogen	Blue Hydrogen	Turquoise Hydrogen	Green Hydrogen
Process	SMR or gasification	SMR or gasification with carbon capture (85-95%)	Pyrolysis	Electrolysis
Source	Methane or coal 	Methane or coal 	Methane 	Renewable electricity 

➤ Features which make it more green:

 _____.

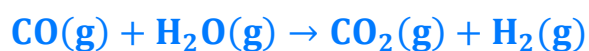
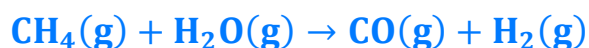
 _____.

Space for Personal Notes



Exploration: Steam Reforming

- Steam: _____.
- Hydrogen Gas can be produced through steam reforming, using methane $\text{CH}_4(\text{g})$:
 1. Methane reacts with steam to produce hydrogen gas and carbon monoxide.
 2. The carbon monoxide can further react to produce more hydrogen gas.



Discussion: What type of hydrogen is steam reforming?

[grey] / [blue] / [turquoise] / [green] hydrogen



Steam Reforming



- Hydrogen Gas is stored as **liquid under high pressure**.
- Process:

$$\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$$

$$\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$$
- Products: _____.
- Methane is currently obtained from fossil fuel, but work is done to obtain it from biogas.
- Type of Hydrogen: [grey] / [blue] / [turquoise] / [green]

Space for Personal Notes

Sub-Section: Polymer Electrolyte Membrane (PEM) Electrolyser



Context

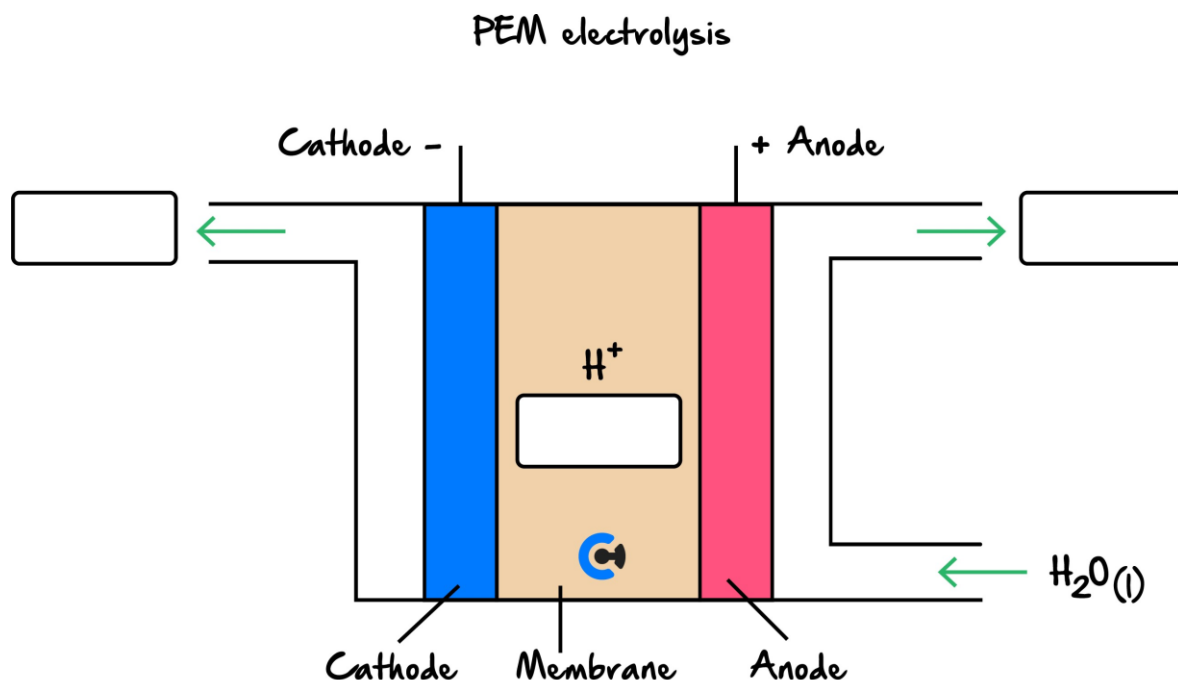
➤ Green Hydrogen Methods in VCAA Study Design:

- 🌐 Polymer electrolyte membrane electrolysis powered by either photovoltaic (solar) or wind energy.
- 🌐 Artificial photosynthesis using a water oxidation and proton reduction catalyst system.

Let's have a look at Polymer Electrolyte Membrane (PEM) Electrolyser powered by either photovoltaic (solar) or wind energy!

Exploration: Polymer Electrolyte Membrane (PEM) Electrolyser

➤ The cell diagram is shown below:



➤ Water in acidic conditions is inputted into the cell and is electrolysed.

➤ Half-Equations:

Cathode	Anode

➤ Overall Reaction: _____.

➤ Products Produced: *(Label Above)*

➤ Electrolyte Movement: *(Label Above)*

➤ The difference with this PEM electrolyser is that it uses a _____ electrolyte.

➤ Electrode Properties: _____.

NOTE: The PEM cell has the same electrode properties as fuel cells.



Polymer Electrolyte Membrane Electrolysis

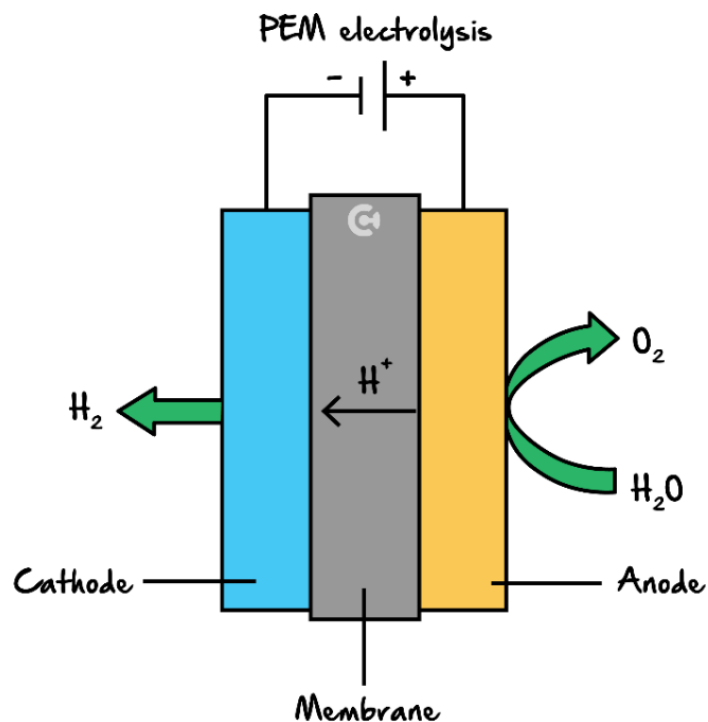
➤ Energy Used: _____.

➤ Electrolyte: _____.

➤ Electrodes: PICCY.

➤ Disadvantage: _____.





➤ Reaction: Electrolysis of _____.

Cathode	Anode

➤ Overall Reaction: _____.

Active Recall: What was the purpose of the membrane?

➤ _____.

➤ _____.

Space for Personal Notes

How does it link to sustainability and green chemistry principles?










Link PEM Electrolyser to Sustainability & Green Chemistry Principles

➤ Sustainable Development Goals:

 Goal 2: Zero Hunger	[Relevant] / [Not Relevant]
 Goal 6: Clean water and sanitation	[Relevant] / [Not Relevant]
 Goal 7: Affordable and clean energy	[Relevant] / [Not Relevant]
 Goal 9: Industry, innovation and infrastructure	[Relevant] / [Not Relevant]
 Goal 11: Sustainable cities and communities	[Relevant] / [Not Relevant]
 Goal 12: Responsible consumption and production	[Relevant] / [Not Relevant]
 Goal 13: Climate action	[Relevant] / [Not Relevant]
 Goal 14: Life Below water	[Relevant] / [Not Relevant]
 Goal 15: Life on land	[Relevant] / [Not Relevant]

➤ Green Chemistry Principles:

 Atom Economy:	[Relevant] / [Not Relevant]
 Catalysis:	[Relevant] / [Not Relevant]
 Design for degradation:	[Relevant] / [Not Relevant]
 Design for energy efficiency:	[Relevant] / [Not Relevant]
 Designing safer chemicals:	[Relevant] / [Not Relevant]
 Prevention of wastes:	[Relevant] / [Not Relevant]
 Use of renewable feedstocks:	[Relevant] / [Not Relevant]

➤ Type of Economy: [Circular] / [Linear]



Discussion: What are the energy conversions in a PEM electrolyser using solar energy?

Space for Personal Notes

Sub-Section: Artificial Photosynthesis

Now, let's have a look at another 'green' production method of hydrogen gas!

Exploration: Reactions

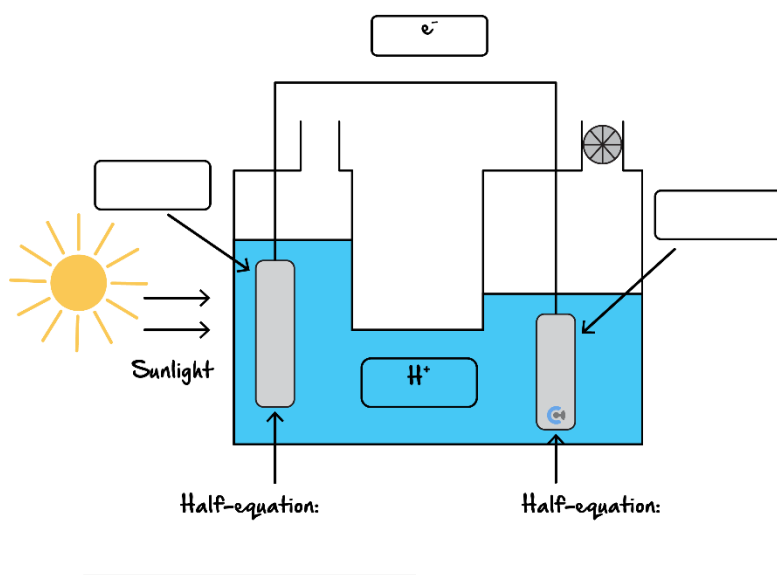
➤ Electrolysis of Acidic Water:

⚙ Half-Equations:

Cathode	Anode

⚙ Overall Equation: _____

- **Type of Energy Inputted:** Instead of electrical energy, _____ energy is inputted instead!
- Sunlight is shone on to the left electrode, causing the water to oxidise.










- **Energy Conversion:** _____.
- **Energy Efficiency:** [High] / [Low]



Link Artificial Photosynthesis to Green Chemistry Principles

➤ Green Chemistry Principles:

 Atom Economy:	[Relevant] / [Not Relevant]
 Catalysis:	[Relevant] / [Not Relevant]
 Design for degradation:	[Relevant] / [Not Relevant]
 Design for energy efficiency:	[Relevant] / [Not Relevant]
 Designing safer chemicals:	[Relevant] / [Not Relevant]
 Prevention of wastes:	[Relevant] / [Not Relevant]
 Use of renewable feedstocks:	[Relevant] / [Not Relevant]

How does the solar energy cause electrolysis?



Protons



➤ Molecular Formula: _____.

Space for Personal Notes



Exploration: Natural Photosynthesis

➤ Reaction:

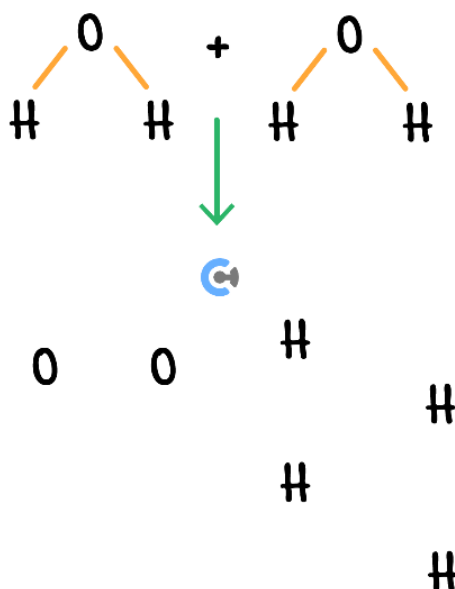


➤ Energy Used: _____.

Two Stages

➤ Stage #1: Light-dependent stage - Energy from light is used to split water into oxygens and protons.

 Structural Formula Reaction:



 Half-Reaction: _____

➤ Stage #2 Light-independent stage - Protons are combined with carbon dioxide to produce glucose.

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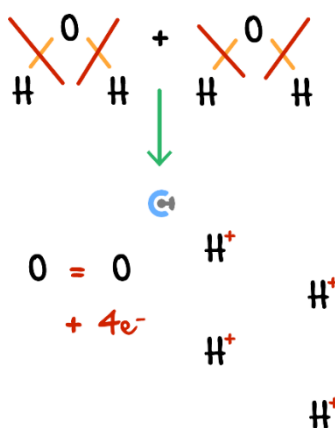
How about artificial photosynthesis?



Exploration: Artificial Photosynthesis

- **Context:** Scientists have tried to replicate this biological process.
- **Stage #1:** Light-dependent stage - Using visible light to split water into oxygens and protons.

🔧 Structural Formula Reaction:

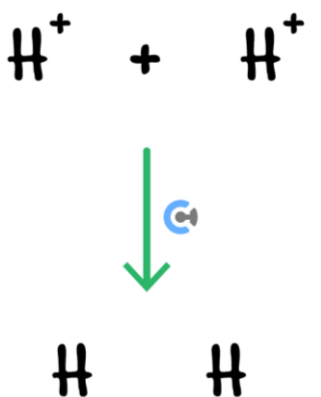


🔧 **Half-Reaction:** $2\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$

🔧 **Catalyst:** _____.

- **Stage #2:** Light-independent stage - Protons are converted to _____ molecules.

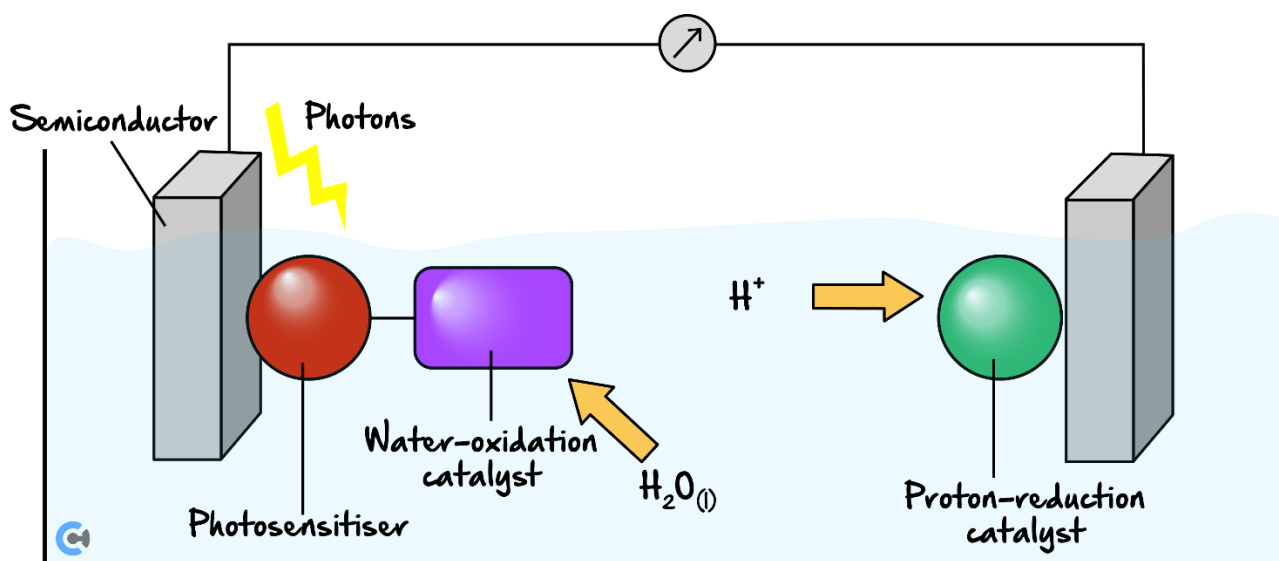
🔧 Structural Formula Reaction:



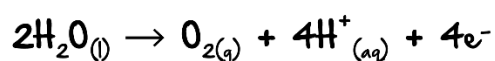
🔧 **Half-Reaction:** _____.

🔧 **Catalyst:** _____.

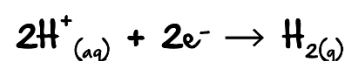
➤ Possible Setup #1:



Oxidation:



Reduction:



➤ Water-oxidation catalyst & Proton-reduction catalyst issues: _____.

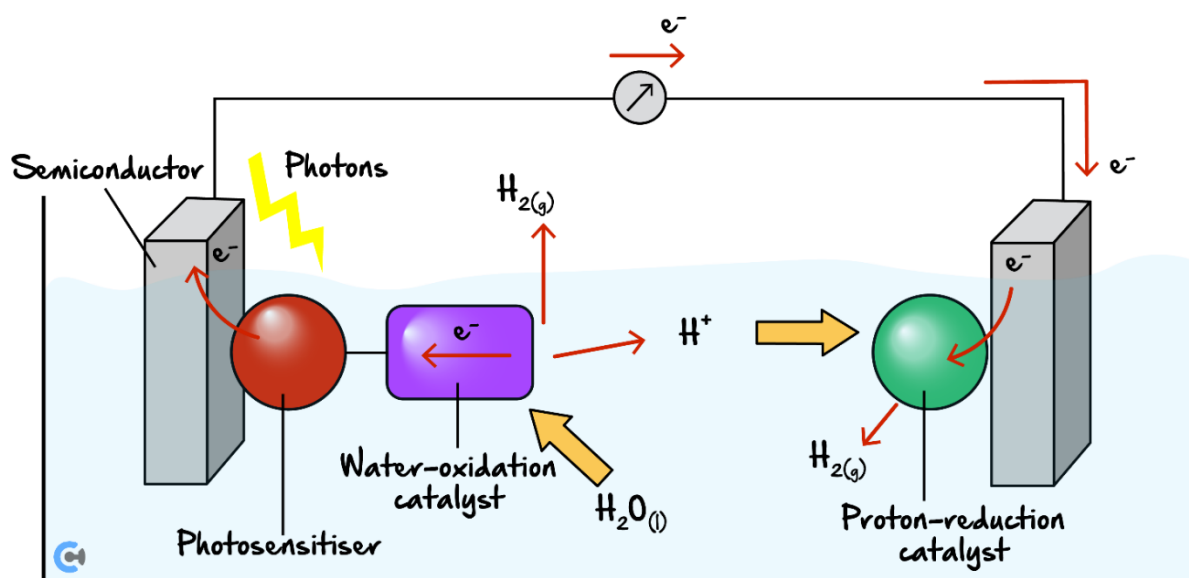
➤ Possible Setups #2 & #3:

Possible Setup #2:	Possible Setup #3:

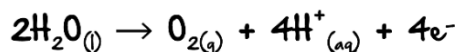
Artificial Photosynthesis Cell

➤ Artificial Photosynthesis Alternative Name:

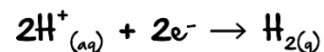
"water oxidation and proton reduction catalyst system"



Oxidation:



Reduction:



➤ Energy Conversion: _____.

➤ Energy Efficiency: [High] / [Low]

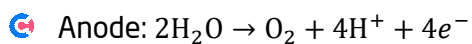
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PEM Electrolyser vs Artificial Photosynthesis Cell

Similarities:

➤ **Reaction:** Electrolysis of _____.



➤ **Energy Used:** _____.

➤ **United Nations Sustainable Development Goals:**

1. Goal _____: _____ – _____.

2. Goal _____: _____ – _____.

3. Goal _____: _____ – _____.

➤ _____.

➤ _____.

➤ **Green chemistry principles:** _____.

➤ **Disadvantages:**

⚡ _____.

⚡ _____.

Differences:

PEM Electrolyser	Artificial Photosynthesis
	<p>Oxidation: $2\text{H}_2\text{O}_{(l)} \rightarrow \text{O}_{2(g)} + 4\text{H}^+_{(aq)} + 4\text{e}^-$</p> <p>Reduction: $2\text{H}^+_{(aq)} + 2\text{e}^- \rightarrow \text{H}_{2(g)}$</p>
Electrolyte:	Electrolyte:
Energy Conversion:	Energy Conversion:
Green Chemistry Principles:	Green Chemistry Principles:

Space for Personal Notes



Try some questions!

Question 18 (7 marks)

Research is done into the production of hydrogen gas, whereby the water oxidation and proton reduction catalyst system is sometimes referred to as ‘artificial photosynthesis’.

- a.**
- i.** Explain why the term water oxidation is appropriate and support your answer with a relevant equation. (1 mark)

 - ii.** Explain why the term proton reduction is appropriate and support your answer with a relevant equation. (1 mark)

 - iii.** State **one** another product other than hydrogen which is produced during this process. (1 mark)

 - b.** State **one** way in which this method of generating hydrogen gas is different from electrolysis using a renewable energy source. (1 mark)

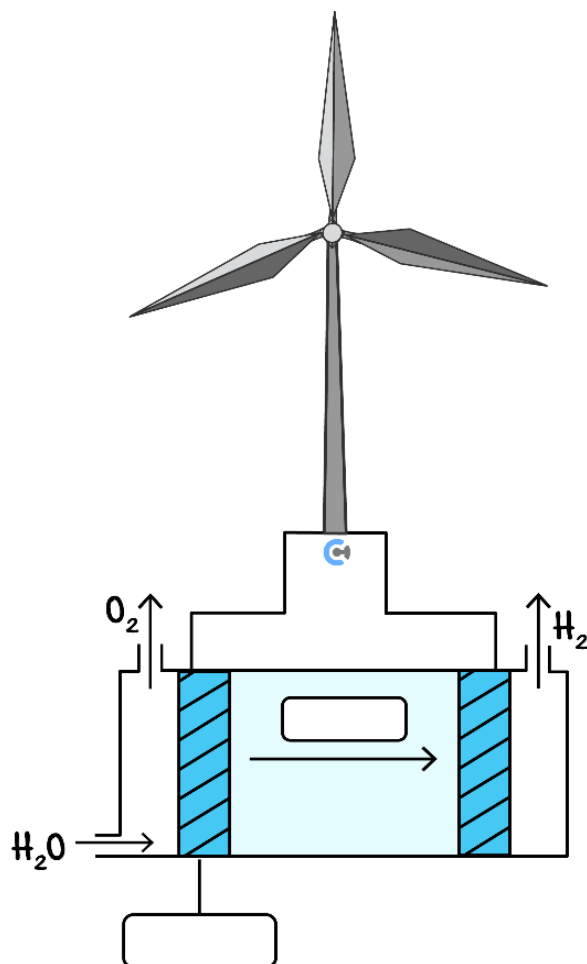
- c. Using **two** relevant sustainable development goals, state **two** major challenges associated with the widespread use of artificial photosynthesis to produce hydrogen gas on a larger scale. Use **item (26) (i)** of the Data Book. (2 marks)

- d. Using a relevant sustainable development goal, state **one** major environmental benefit that this process could have if it is adopted on a large scale. Use **item (26) (i)** of the Data Book. (1 mark)

Space for Personal Notes

Question 19 (4 marks)

The following diagram shows a polymer electrolyte membrane electrolysis cell (PEM) which is used to produce hydrogen gas in a 'green' manner. This particular cell uses wind energy.



- a. Label the electrolyte in the diagram above. (1 mark)
- b.
 - i. Label the left electrode as the cathode or anode in the box provided above. (1 mark)
 - ii. Write the half-reaction which occurs at the negative electrode. (1 mark)

- c. State **one** disadvantage of a PEM electrolyser. (1 mark)



Contour Check

- ☐ **Learning Objective: [2.2.1] - Find electrolytic reactions in non-standard conditions (molten & high concentration)**

Study Design

“use and limitations of the electrochemical series to explain or predict the products of the electrolysis of particular chemicals, given their state (molten liquid or in aqueous solution) and the electrode materials used, including the writing of balanced equations (with states) for the reactions occurring at the anode and cathode and the overall redox reaction for the cell”

Key Takeaways

☐ **High Concentration:**

- ☐ Chloride ions at concentrations greater than _____ concentration become a [stronger] / [weaker] reductant and [react] / [do not] react in preference to water.
- ☐ Sodium ions are concentrations greater than 4.0 M concentration [react] / [do not] react in preference to water.

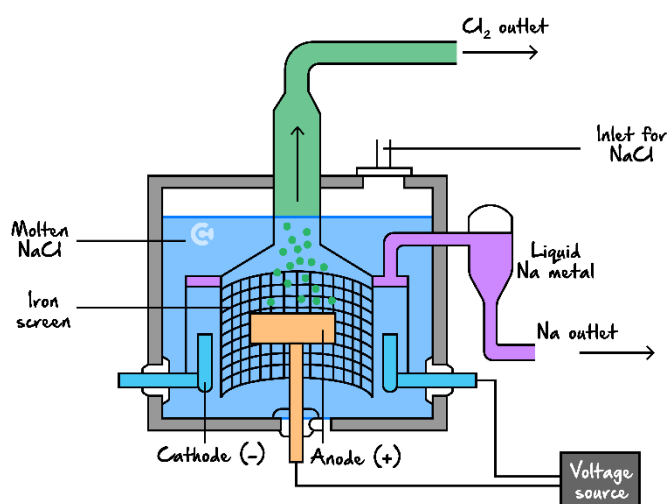
☐ **Molten Concentration:** _____ is not present, and the state of ions is _____.

Learning Objective: [2.2.2] - Identify features of electrolytic cells & their purpose

Study Design

"the common design features and general operating principles of commercial electrolytic cells (including, where practicable, the removal of products as they form), and the selection of suitable electrode materials, the electrolyte (including its state) and any chemical additives that result in a desired electrolysis product (details of specific cells not required)"

Key Takeaways



- ☐ Molten Electrolyte Purpose: _____.
- ☐ Iron at the cathode: _____.
- ☐ Other Electrolytes (e.g., CaCl_2) added: _____.
- ☐ Barrier within the cell:
 - ☐ _____.
 - ☐ _____.
- ☐ Products constantly removed:
 - ☐ _____.
 - ☐ _____.

Enclosed container: _____.

Learning Objective: [2.2.3] - Identify key features, write reactions & relate to sustainability & green chemistry principles regarding production of green hydrogen (PEM & Artificial Photosynthesis)

Study Design

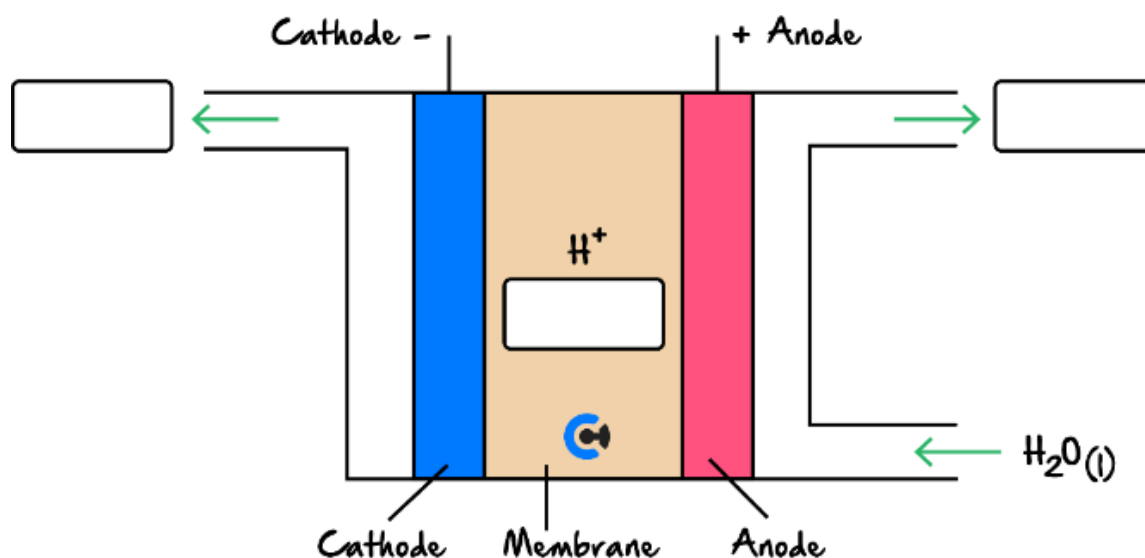
“the role of innovation in designing cells to meet society’s energy needs in terms of producing ‘green’ hydrogen (including equations in acidic conditions) using the following methods:

- ☐ polymer electrolyte membrane electrolysis powered by either photovoltaic (solar) or wind energy;
- ☐ artificial photosynthesis using a water oxidation and proton reduction catalyst system”

Key Takeaways

- ☐ Both PEM electrolyser & artificial photosynthesis involve electrolysis of _____.
- ☐ PEM Electrolyser:

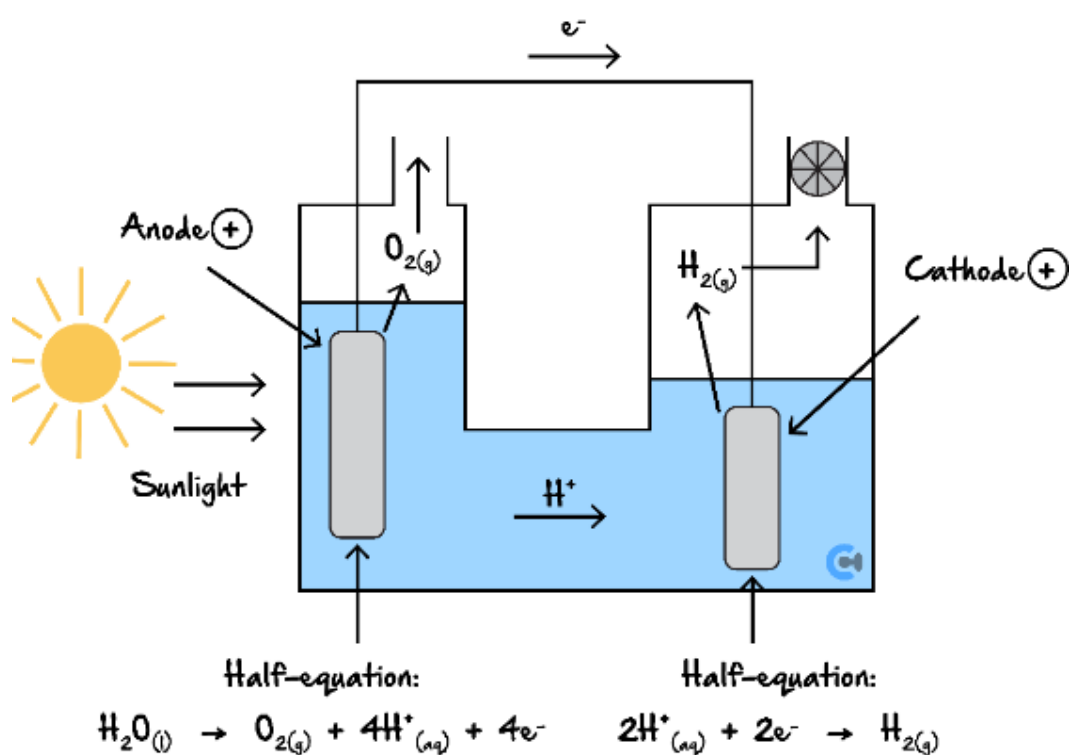
PEM electrolysis



Cathode	Anode

- Energy Used: _____.
- Green Chemistry Principle: _____.

□ Artificial Photosynthesis:



- Energy Conversion: _____.
- Green Chemistry Principle: _____.



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VCE Chemistry $\frac{3}{4}$

Free 1-on-1 Support



Be Sure to Make The Most of These (Free) Services!

- Experienced Contour tutors (45+ raw scores, 99+ ATARs).
- For fully enrolled Contour students with up-to-date fees.
- After school weekdays and all-day weekends.

<u>1-on-1 Video Consults</u>	<u>Text-Based Support</u>
<ul style="list-style-type: none">➤ Book via bit.ly/contour-chemistry-consult-2025 (or QR code below).➤ One active booking at a time (must attend before booking the next).	<ul style="list-style-type: none">➤ Message +61 440 137 304 with questions.➤ Save the contact as "Contour Chemistry".

Booking Link for Consults

bit.ly/contour-chemistry-consult-2025



Number for Text-Based Support

[+61 440 137 304](tel:+61440137304)