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# VCE Chemistry ¾ Features of Electrolytic Cells [2.2]

Workbook

### Outline:

Non-Standard Conditions  Higher Concentrations  Molten Conditions  Features of Electrolytic Cells  Commercial Cell - Down's Cell  Molten Electrolyte  Material of Electrode  Other Electrolytes Added  Barrier Within Cell  Constantly Removing Products	Pg 2-21	Safety and Storage of Hydrogen Gas  Safety of Hydrogen Gas  Storage of Hydrogen Gas  Production of Hydrogen Gas  Production of Hydrogen Gas  Production of Hydrogen Gas  Polymer Electrolyte Membrane (PEM) Electrolyser  Artificial Photosynthesis	
<ul> <li>Constantly Removing Products</li> <li>Enclosed Container</li> </ul>		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?

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- > SC

#### **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!



## **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)

<u>Reaction</u>		Standard Electrode Potential  (E°) In Volts At 25°C
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(1)$		+1.77
$\operatorname{Cr}_2 \operatorname{O}_7^{2-}(\operatorname{aq}) + 14\operatorname{H}^+(\operatorname{aq}) + 0$	$6e^- \rightleftharpoons 2Cr^{3+}(aq) + 2H_2O(l)$	+1.36
$Cl_2(g) + 2e^-$	<b>⇒</b> 2Cl <sup>-</sup> (aq)	+1.36
$O_2(g) + 4H^+(aq)$	+ 4e <sup>-</sup> (2H <sub>2</sub> O(l)	+1.23
$Br_2(l) + 2e^-$	⇌ 2Br <sup>-</sup> (aq)	+1.09
$\operatorname{Zn}^{2+}(\operatorname{aq}) + 2$	$2e^- \rightleftharpoons \operatorname{Zn}(s)$	-0.76
$2H_2O(1) + 2e^- \rightleftharpoons I$	$I_2(g) + 20H^-(aq)$	-0.83
$Mn^{2+}(aq) + 2$	$e^- \rightleftharpoons \operatorname{Mn}(s)$	-1.18
Al <sup>3+</sup> (aq) + 3	$Be^- \rightleftharpoons Al(s)$	-1.66
$Mg^{2+}(aq) + 1$	$2e^- \rightleftharpoons Mg(s)$	-2.37
Na <sup>+</sup> (aq) + 0	e⁻ ⇌ Na(s)	-2.71
Ca <sup>2+</sup> (aq) + 2	2e⁻ ⇌ Ca(s)	-2.87



#### Reactions Which Occur:

Strongest Oxidant:	Strongest Reductant:
Cathode (Reduction) Half-Equation:	Anode (Oxidation) Half-Equation:
24h0+2e->+2+2045	24ho-302+4474/

## **Discussion:** Relative Oxidant/Reductant Strength



<u>R</u>	<u>eaction</u>	Standard Electrode Potential  (E°) In Volts At 25°C
$H_2O_2(aq) + 2H^4$	$(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.77
$\operatorname{Cr}_2 \operatorname{O}_7^{2-}(\operatorname{aq}) + 14 \operatorname{H}^+(\operatorname{aq})$	$+6e^- \rightleftharpoons 2\mathrm{Cr}^{3+}(\mathrm{lq}) + 2\mathrm{H}_2\mathrm{O}(\mathrm{l})$	+1.36
$Cl_2(g) + 2$	$2e^{-} \rightleftharpoons 2Cl^{-}(aq)$	+1.36
$O_2(g) + 4H^+(a)$	$q) + 4e^{-} = 2H_2O(h)$	+1.23
$Br_2(l) + 2$	$2e^- \rightleftharpoons 2Br^-(aq)$	+1.09
Zn <sup>2+</sup> (aq)	$+2e^- \rightleftharpoons \operatorname{Zn}(s)$	-0.76
$2H_2O(I) + 2e^{-}$	$\stackrel{\rightleftharpoons}{=} H_2(g) + 20H^-(aq)$	-0.83
Mn <sup>2+</sup> (aq)	$+2e^- \rightleftharpoons Mn(s)$	-1.18
Al <sup>3+</sup> (aq)	$-3e^- \rightleftharpoons Al(s)$	-1.66
Mg <sup>2+</sup> (aq)	$+2e^- \rightleftharpoons Mg(s)$	-2.37
Na <sup>+</sup> (aq	$+e^- \rightleftharpoons Na(s)$	-2.71
Ca <sup>2+</sup> (aq)	$+2e^- \rightleftharpoons Ca(s)$	-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

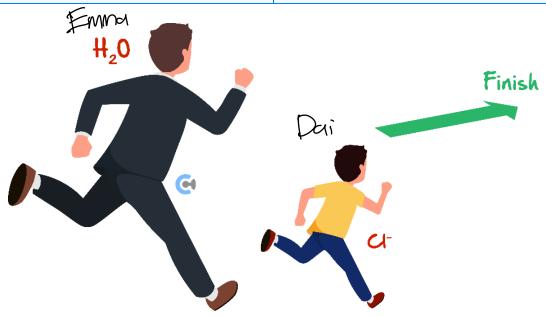
## Consider the following analogy!



## Analogy: Pushing in Line to Reach the Finish I

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

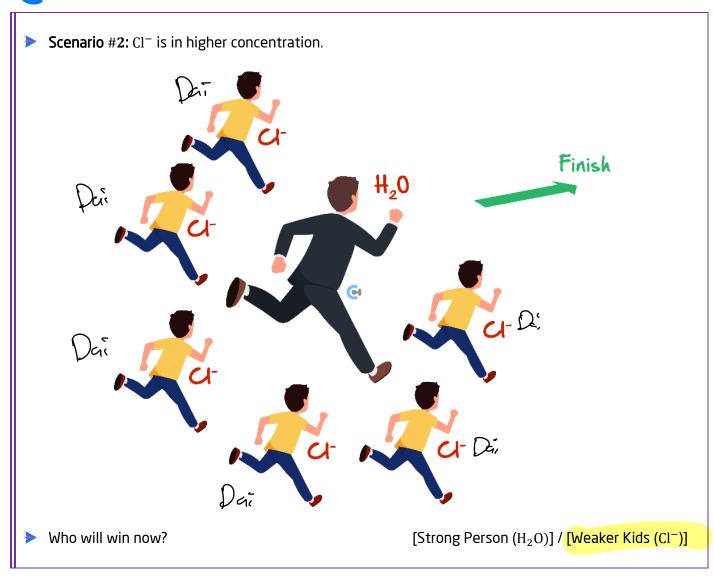
H <sub>2</sub> O(1)	<u>Cl<sup>-</sup>(aq)</u>
Huge Strong Person	Little Kid



Who will win?

[Strong Person (H<sub>2</sub>O)] / [Weaker Kid (Cl<sup>-</sup>)]

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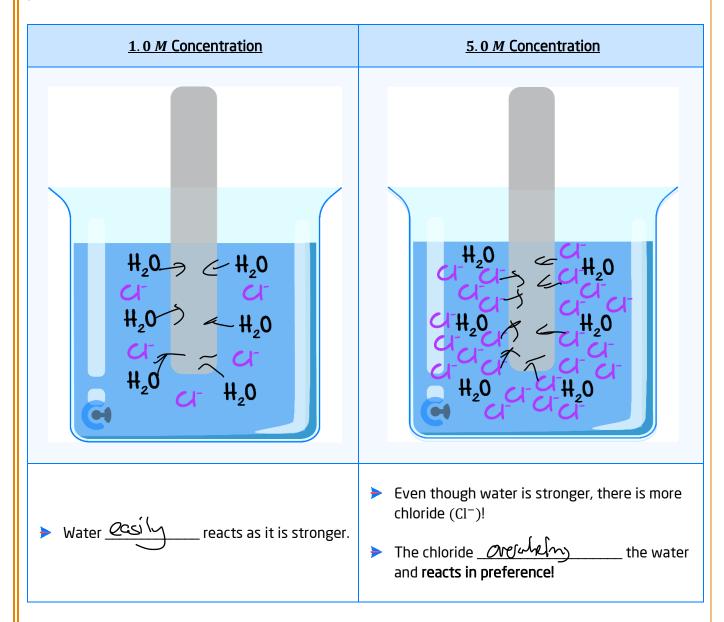


## Let's link that to actual electrolysis now!



#### Exploration: 1.0 M vs 5.0 M Concentration

Water & chloride at different concentrations:





## How about Na+?



#### Analogy: Pushing in Line to Reach the Finish II

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

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6

H <sub>2</sub> O(l)	<u>Na<sup>+</sup>(aq)</u>
Huge Strong Person	Ant



Who will win?

[Strong Person (H<sub>2</sub>O)] / [Ant (Na<sup>+</sup>)]

Scenario #2: Na+ is in higher concentration.



Who will win now?

[Strong Person (H<sub>2</sub>O)] / [Ants (Na<sup>+</sup>)]

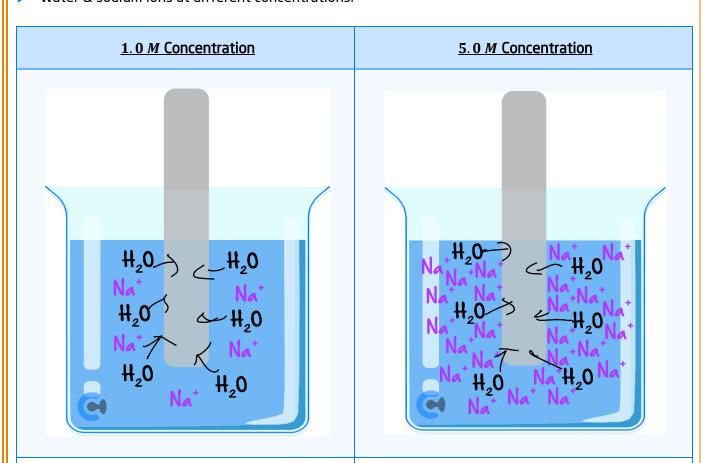


## Let's link that to actual electrolysis now!



#### Exploration: Sodium Ions (Na<sup>+</sup>) at 5.0 M Concentration

Water & sodium ions at different concentrations:



- Water <u>easin</u> reacts as it is stronger.
- Even though there are more sodium ions (Na<sup>+</sup>), water is significantly stronger!
- > Water still rest in professe to sodium ions!





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



### **Exploration**: Electrolysis of NaCl at Higher Concentrations

No.

- 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)

Reaction	Standard Electrode Potential (E°) In Volts At 25°C	
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.77	
$Au^+(aq) + e^- \rightleftharpoons Au(s)$	+1.68	
$Cl_2(g) + 2e^{-}$ $\rightleftharpoons$ $2Cl^-(aq)$	+1.36	
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23	
$Br_2(l) + 2e^{-} \rightleftharpoons 2Br^{-}(aq)$	+1.09	
$Ag^{+}(aq) + e^{-} \rightleftharpoons Ag(s)$	+0.80	
Fe <sup>2+</sup> (aq) + 2 $e^- \rightleftharpoons$ Fe(s)	-0.44	
$\operatorname{Zn^{2+}}(\operatorname{aq}) + 2e^{-} \rightleftharpoons \operatorname{Zn}(\operatorname{s})$	-0.76	
$2H_2O(1) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	-0.83	
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	-1.18	
$Al^{3+}(aq) + 3e^{-} \rightleftharpoons Al(s)$	-1.66	
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	-2.37	
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71	
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	-2.87	



Cathode (Reduction) Half-Reaction	Anode (Oxidation) Half-Reaction
24/2011e-34/2420H	2CT->C/2+2E



<u>Extension:</u> 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  $(H_2O)$ :

Reaction	Standard Electrode Potential  (E°) In Volts At 25°C
$Cl_2(g) + 2e^{-}$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23
$2H_2O(1) + 2e^- \Rightarrow H_2(g) + 2OH^-(aq)$	-0.83
$\operatorname{Mn^{2+}}(\operatorname{aq}) + 2e^{-} \rightleftharpoons \operatorname{Mn}(s)$	-1.18
$Al^{3+}(aq) + 3e^{-} \rightleftharpoons Al(s)$	-1.66
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	-2.37
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71

What is the difference in EMF between:

Chloride (CI) And Water (H <sub>2</sub> O)	Sodium lons (Na+) And Water (H <sub>2</sub> O)
0.137	~2V



#### **Electrolysis of NaCl at Higher Concentrations**



<u>Conditions</u>	Sodium ions (Na <sup>+</sup> )	<u>Chloride (Cl<sup>-</sup>)</u>
1.0 <i>M</i> Concentration	[slightly] / [significantly] weaker oxidant than water	[slightly] / [significantly] weaker reductant than water
4.0 M Concentration	[will] / <mark>[will not<b>] reduce</b> in preference to water</mark>	[will] / [will not] <b>oxidise</b> in preference to water

- Cutoff for "High Concentration": >3.0 M.
- Note: Only \_\_\_\_\_ at high concentration is mainly tested!
- **Additional Information**: As Cl<sup>-</sup>(aq) is very close in reductant strength to water at most concentrations (1.0 M - 5.0 M), chloride and water are oxidising **simultaneously**!

1.0M

#### Your turn!



#### **Question 1**

The electrolysis of 5.0 M concentration of calcium chloride (CaCl<sub>2</sub>(aq)) is undertaken with inert electrodes.

Write the half-equations which occur at the:

a. Positive electrode.

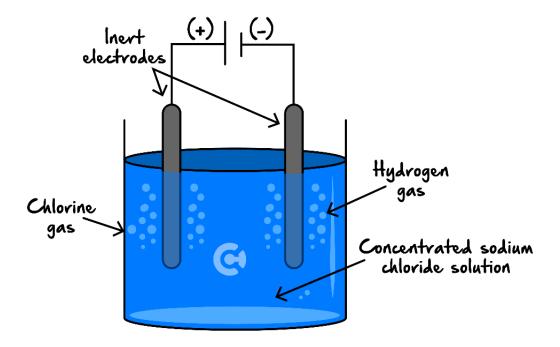
201 ) (1) + let (92) (7) more basic b. Negative electrode. ORC

2th0+2e->th+20+1



#### **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:

- 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<sup>+</sup> ions
- **B.** Water molecules
- C. Cl<sup>-</sup> ions
- **D.**  $O_2$  molecules



Question	4	Additional	(	Duestion.
Question	7	Tuuliuullai	•	, ucsuon.

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

- High concentrations always cause halide ions to oxidise in preference to water.
- 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?** 



lava

#### **Molten**



\_temperatures,

<u>Discussion:</u> Is water present in molten conditions?



[Yes] <mark>/ [No] /</mark> [Maybe]



## **CHONTOUREDUCATION**

#### **Context**



In the previous section, can sodium ions react even at higher concentrations?



What reacts in preference? \_\_\_\_\_\_\_\_\_

In molten conditions, is this water present?



**Conclusion**: Molten Conditions are used to react everything which is weaker than water!

<u>Reaction</u>	Standard Electrode Potential  (E°) In Volts At 25°C
$Fe^{2+}(aq) + 2e^{-} \rightleftharpoons Fe(s)$	-0.44
$Zn^{2+}(aq) + 2e^{-} \rightleftharpoons Zn(s)$	-0.76
$2e^- \rightleftharpoons H_2(g) + 20H^-(aq)$	-0.83
$Mn^{2+}(aq) + 2e^{-} \rightleftharpoons Mn(s)$	-1.18
$Al^{3+}(aq) + 3e^{-} \rightleftharpoons Al(s)$	-1.66
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	-2.37
Owg 97 $Na^+(q) + e^- \rightleftharpoons Na(s)$	-2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	-2.87
$K^+(aq) + e^- \rightleftharpoons K(s)$	-2.93
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	-3.04







Question 5 Walkthrough.

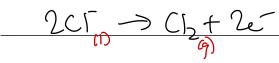
Potassium chloride is electrolysed using an cathode and a graphite anode at molten conditions.

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

a. Cathode.

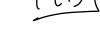


**b.** Anode.



<u>Discussion:</u> What is the state of potassium ions  $(K^+)$  at molten conditions?

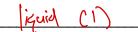




#### **Non-Standard Condition Reactions**



- At **higher concentrations**, chloride ions (Cl<sup>-</sup>) react in preference to water.
- **Molten Conditions:** 
  - Water [is] / [is not] present!
  - 😉 State of cations/anions are **not aqueous (aq)**, but instead are \_\_\_\_\_\_ட்டிய்ல் ட்டி





## Your turn!



#### **Question 6**

Molten calcium fluoride (CaF<sub>2</sub>) is electrolysed using a cobalt cathode and a graphite anode.

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

(a<sup>2f</sup><sub>(1)</sub> + 2e<sup>-</sup>) (a<sub>(S/1)</sub>

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

2F (1) -> F2 (5) + 2e-

#### **Question 7**

A molten mixture of manganese fluoride is electrolysed.

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

Motintle -> Mossi)

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

2Fin -> Fig +2i

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



$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$$



## Try some more questions!



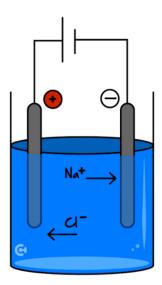
#### **Question 8**

A molten mixture of equal parts aluminum fluoride, AlF<sub>3</sub>, and sodium chloride, NaCl, undergoes electrolysis. Which one of the following statements about this reaction is correct?

- Sodium metal will be produced at the cathode and fluorine gas will be produced at the anode.
- 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.
- 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)

myexam

Inspired from VCAA Chemistry Exam 2021

2:5/5

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.

In aguou carditions, water is present, the reduces in preface to ICT.

: Molta carditions must be used to eliminate competition of water.

As a result, this hard-eg of authode 241,0-12e->+12+20+100

longer occurs

new ey: Ktoste -> Kg1)

> power surve is added to input to

The real moles, reaction to occur.

inert cheshods used so other

cellans or high top.

ocur.

Kt (1) +e > K (5/1) 2CT (1) > (1/29) +2-

CH34 [2.2] - Features of Electrolytic Cells - Workbook

KC (1)

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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, PbBr<sub>2</sub>(l).
- **D.** Copper sulphate,  $CuSO_4(aq)$ .

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## Section B: Features of Electrolytic Cells

#### Sub-Section: Commercial Cell - Down's Cell

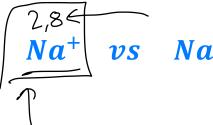


Now that we've looked at how to predict the reactions which occur, let's have a look at some electrolytic cells in real life!

Discussion: Will sodium generally exist in its ion form (Na+) or metal form (Na) in nature when it is



mined from the ground?





<u>Discussion:</u> 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?





- **Electrolysis Purpose**: Produces products unlikely to exist in nature.
- **Example:** Down's Cell is used to produce pure sodium metal.

electrolysu

Relevance: While not explicitly in the study design, understanding its construct is useful as commercial cell features are tested.



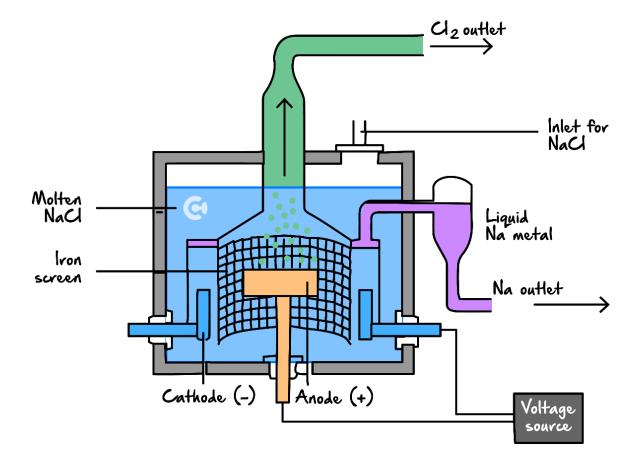


## Let's look at Down's Cell Together!

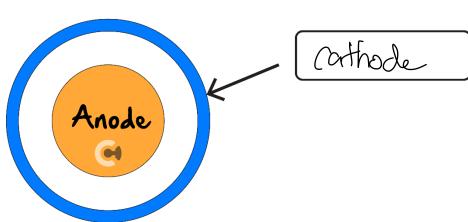
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#### **Exploration**: Down's Cell

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







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



**Equations:** 

Cathode (Reduction) Half-Reaction	Anode (Oxidation) Half-Reaction
(Nationte > Nam)XZ	2c/m->c/29+2c

- © Overall Reaction: 2Nacl 32Nafc[2 (5)
- **Equations:**

Anode (+): 
$$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$$

Cathode (-): 
$$Na^+(l) + e^- \rightarrow Na(l)$$

Overall: 
$$2NaCl(l) \rightarrow 2Na(l) + Cl_2(g)$$



## **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>	Cathode Reaction	Anode Reaction
1.0 <i>M</i> NaCl	$H_2O(l) \rightarrow H_2(g)$	$H_2O(l) \rightarrow O_2(g)$
4.0 M NaCl	$H_2O(l) \rightarrow H_2(g)$	$Cl^-(aq) \to Cl_2(g)$
Molten NaCl	$Na^+(l) \rightarrow Na(s)$	$Cl^-(l) \to Cl_2(g)$

Reason for Using Molten NaCl: Otherspecies weakenthon water.

## Molten Electrolyte Purpose

To react with species weaker than water.





## **Sub-Section: Material of Electrode**



**Exploration**: Electrode Material

In Down's Cell:



Anode Material	Cathode Material
graphik	1001

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

expersive

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

<u>Reaction</u>	Standard Electrode Potential  (E°) In Volts At 25°C
$Cl_2(g) + 2e^{-} \rightleftharpoons 2Cl^-(aq)$	+1.36
$Br_2(l) + 2e^+ \rightleftharpoons 2Br^-(aq)$	+1.09
$\operatorname{Co}^{2+}(\operatorname{aq}) + 2e^{-} \rightleftharpoons \operatorname{Co}(\operatorname{s})$	-0.28
$Fe^{2+}(aq) + 2e^{-} Fe(s)$	-0.44

- @ Reasoning: Cathole wreachire onyway.
- Question: Why do we use iron used instead of graphite at the cathode?





#### **Electrode Material**



Platinum Electrodes not used: <u>explosive</u>

Iron used at cathode: <u>cathode</u> uneactive

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## **Sub-Section**: Other Electrolytes Added

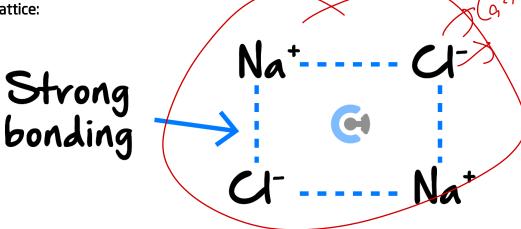


#### **Exploration**: Electrolyte

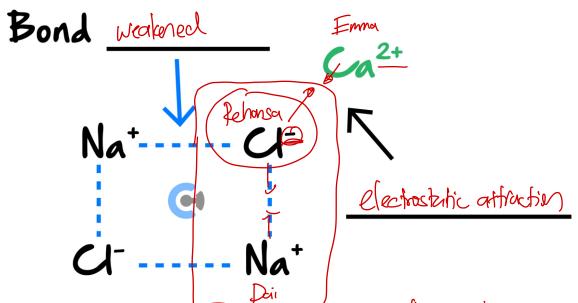
- Electrolyte of Down's Cell is comprised of both molten NaCl(l) and CaCl<sub>2</sub>(l).
- ► Melting point of pure molten NaCl (l): ~ 800°.

Why do we add Ca<sup>2+</sup> ions?

NaCl ionic lattice:



NaCl ionic lattice with Ca<sup>2+</sup> ions are added:



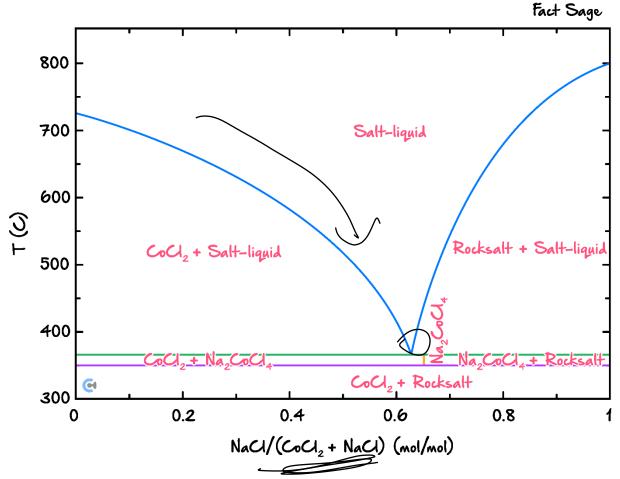
- between the Na<sup>+</sup> and Cl<sup>-</sup>.
- > **Result**: This lowers the melting point of the molten NaCl (I) to roughly \_\_\_\_\_\_.





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

CoU<sub>2</sub> - NaU, 1 atm Data from FTsalt - FACT salt databases

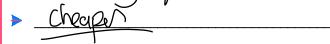


- Effect of Ca<sup>2+</sup> addition: Weakens NaCl ionic bonding, lowering melting point.
- Colligative property: NaCl dissolves in molten CaCl<sub>2</sub>, reducing melting point.
- **Entropy increase:** Ca<sup>2+</sup> disperses particles, increasing randomness.

<u>Discussion:</u> What are the benefits of lowering the overall melting point of the electrolytic cell?



> less every regulared to maintain molter





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

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

**Reasoning**:  $Ca^{2+}$  is <u>weak</u> on the electrochemical series than  $Na^{+}$ , and thus, will not reduce in preference.

[yes] /([no])/ [maybe]

## **Adding Other Electrolytes**



- > Other Electrolytes (e.g. CaCl<sub>2</sub>) are added to lower melfing point.
- > Advantages: Reduce energy required, cost.

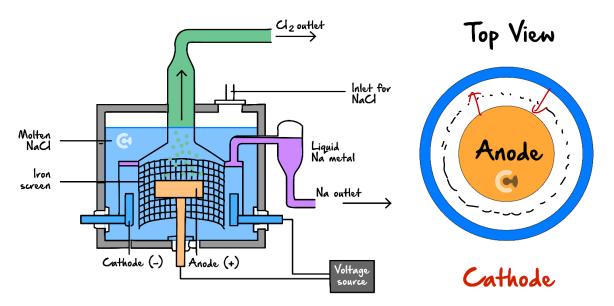


## **Sub-Section: Barrier Within Cell**



#### **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 (Cl<sub>2</sub>(g) and Na(l)).

Reaction	Standard Electrode Potential  (E°) In Volts At 25°C		
$\boxed{\text{Cl}_2(g) + 2e^- \rightleftharpoons 2\text{Cl}^-(aq)}$	+1.36		
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23 V		
$Mg^{2+}(aq) + 2e \rightleftharpoons Mg(s)$	-2.37		
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71		



$\underline{\operatorname{Cl}_2(\mathbf{g})}$	<u>Na(l)</u>
[strong] / [weak] oxidant	[strong] / [weak] reductant

- 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.

  - lon passing through purpose:



complete in knal circuit mointain electric neutrolity

### Barrier Within Electrolytic Cell



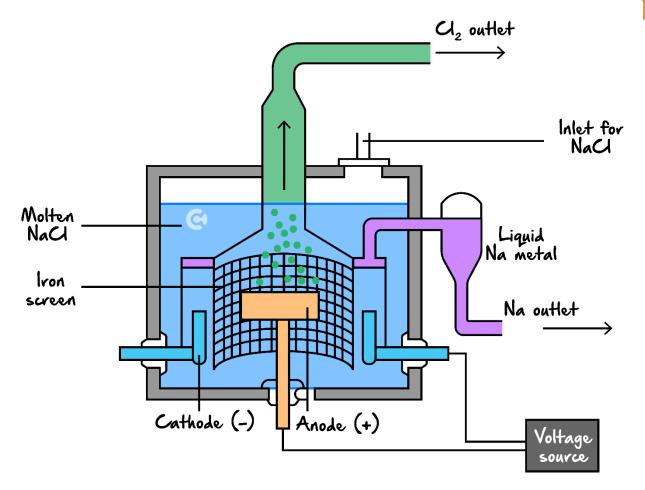
- Purpose:
  - **©** To separate products to prevent direct contact and spontaneous redox reaction.
  - Allow flow of ions.



## **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? products

# Definition

## **Constantly Removing Products**

- Purpose:
  - To reduce chance of products coming In contact with one another and reacting back.
  - To prevent <u>birldrup</u> products which may intitle with reaction.

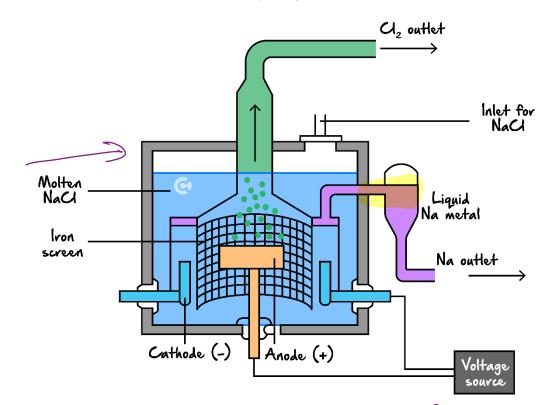


## **Sub-Section:** Enclosed Container



#### **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(1))?

	· · · · · · · · · · · · · · · · · · ·
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( Are lexiles	

Reaction	Standard Electrode Potential (E°) In Volts At 25°C
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$0_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(1)$	+1.23 V
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	-2.37
$Na^{+}(aq) + e^{-} \rightleftharpoons Na(s)$	-2.71

## **C**ONTOUREDUCATION

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

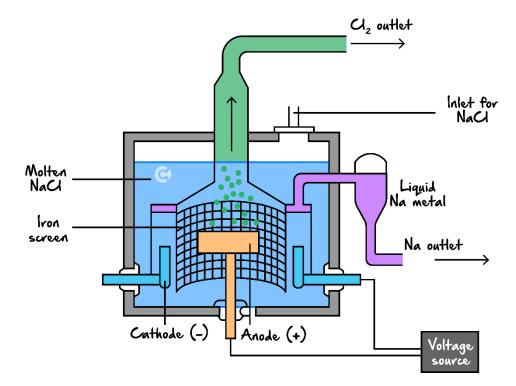
#### **Enclosed Container**



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<sub>2</sub>) 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 0<sub>2</sub> from outside reacting spontaneously.



## Try applying these to different cells!



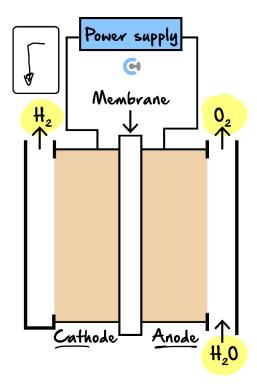
Question 13 (5 marks)



Inspired from VCAA Chemistry Exam 2022

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

Hydrogen, H<sub>2</sub>, 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)

Electrons flow from anoth -> contrade.

Anoth loses e - (oxidation tales place) which is saired out contrade.

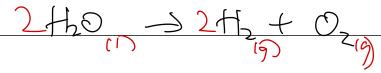
**b.** State **two** functions of the membrane. (2 marks)

- allows flow ions, which maintains electrical neutrality
- prevent products (ffz 202) from coming in contract

Lexploding)



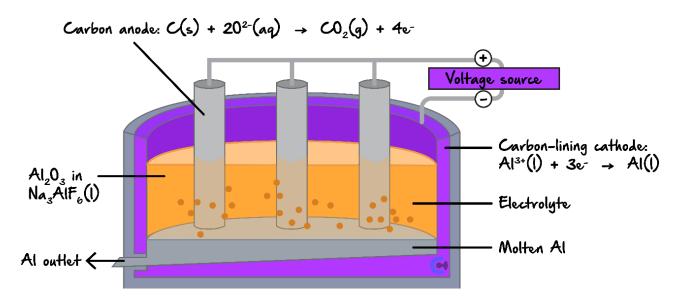
Write the overall equation for the reaction that takes place in the acidic electrolyser shown in the diagram above when it is operating at 80°C. (1 mark)



#### **Question 14**

The Hall-Heroult cell involves the electrolysis of molten aluminum oxide (Al<sub>2</sub>O<sub>3</sub>).

A diagram of the cell is provided below:



The reactions which take place are the following:

Anode: 
$$C(s) + 20^{2-}(l) \rightarrow CO_2(g) + 4e^{-}$$

Cathode: 
$$Al^{3+}(l) + 3e^{-} \rightarrow Al(l)$$

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

All is constantly pumped out to reduce chance for it to come in contact with other products (CO2) and spontaneously reacting. Avoid interference with cell.

# **C**ONTOUREDUCATION

A solution of cryolite (Na <sub>3</sub> AlF <sub>6</sub> ) 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.		
Cryolite is added to lower the melting point of Al2O3. This helps with operation with the cell as less energy is		
required to maintain molten state, and thus saving energy and money.		

#### **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.



# **C**ONTOUREDUCATION

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# Section C: Safety and Storage of Hydrogen Gas

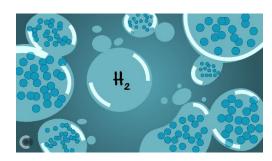
# **Sub-Section**: Safety of Hydrogen Gas



#### **Context**

There are issues with safety surrounding hydrogen gas.





- How does hydrogen gas look like? \_\_\_\_\_\_\_\_
- 🕨 How does hydrogen gas **smell** like? <u>യിയിട്ട</u>
- 🕨 How does hydrogen gas taste like? <u>ধ্রিন্দুরি</u>

# Why is this an issue?

# A

#### **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 difficult to defect



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



gas detector

# Why is hydrogen gas dangerous?



**Exploration**: Why Else Is Hydrogen Gas Dangerous Then?

- Hydrogen Gas Exploding in Air Video:

https://youtu.be/nLuOM9aOWvk?si=0LC2nSIRpo-46RNw&t=45



<u>Discussion:</u> Why is hydrogen gas being flammable dangerous in a car?





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



Safety Precaution	<u>Execution</u>
Ignition Protection	keep away from ignition source
Removal of Combustible Vapours	well-ventilated area
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.





# 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.

2H, O(1) + 2e-> H, cg) + 20H (ca)

**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.

Hzg is being produced. Flammale



# **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?
  - @ can store more in some volume
  - caster to transport

- **Scenario**: Boiling point of hydrogen gas is very low  $(-250^{\circ}\text{C})$ .
- Issue: Hard to turn it into a liquid.
- Method to turn  $H_2(g) \rightarrow \text{Liquid}$  without lowering the temp. to  $-250^{\circ}\text{C}$ :

Storage Pressure Conditions of  $H_2(g)$ :  $\sim 70,000$   $\circlearrowleft$ 

### Storage of Hydrogen Gas

- Hydrogen Gas is stored as liquid under high pressure.
- Reasoning:
  - e essivto transport.

    Store more in some volume.

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



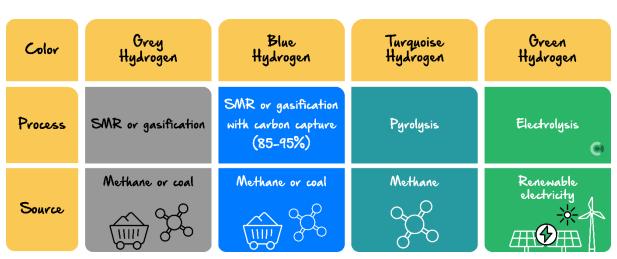
**Discussion:** How Is Hydrogen Gas Produced?

- > electrolysis of water
- > stom retorning



#### **Context**

Production of Hydrogen is ranked on a scale:



- Features which make it more green:
  - rewable
  - @ no greenhouse ops evisulers

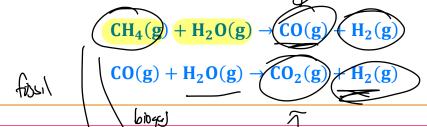


# **CONTOUREDUCATION**

## **Exploration:** Steam Reforming



- Steam: 12019.
- Hydrogen Gas can be produced through steam reforming, using methane CH<sub>4</sub>(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.



<u>Discussion:</u> What type of hydrogen is steam reforming?



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

# Steam Reforming



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

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

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

- Methane is currently obtained from fossil fuel, but work is done to obtain it from biogas.
- Type of Hydrogen (grey] / [blue] / [turquoise] / [green]



# Sub-Section: Polymer Electrolyte Membrane (PEM) Electrolyser



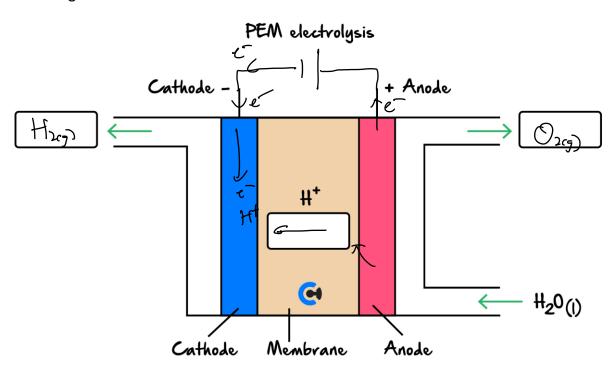
#### **Context**

- 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





- 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

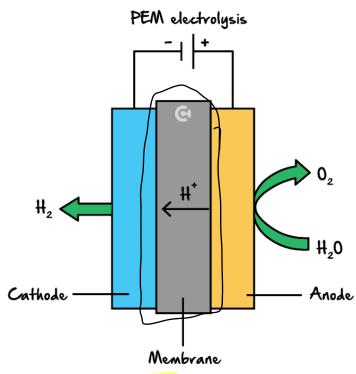


> Electrolyte: <u>、ら</u>い



- Electrodes: PICCY.
- Disadvantage: <u>Expensive</u>





> Reaction: Electrolysis of acids Wall.

<u>Cathode</u>	<u>Anode</u>
2thante - thay	2tholen > Ozy fuffantre

▶ Overall Reaction: 21500 → 3572156

# Active Recall: What was the purpose of the membrane?

- ?
- > allow ions to pasthough maintain electric reutrality
- > prevents product from spon reacting



# How does it link to sustainability and green chemistry principles?





#### <u>Link PEM Electrolyser to Sustainability & Green Chemistry Principles</u>

- 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 Scholind Severalle [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]



<u>Discussion:</u> What are the energy conversions in a PEM electrolyser using solar energy?



solar -> efectric -> chenical

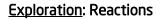
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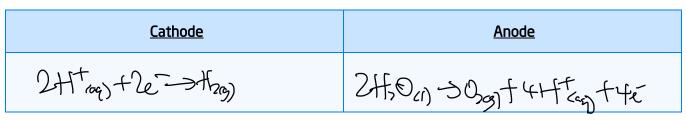
# **Sub-Section**: Artificial Photosynthesis



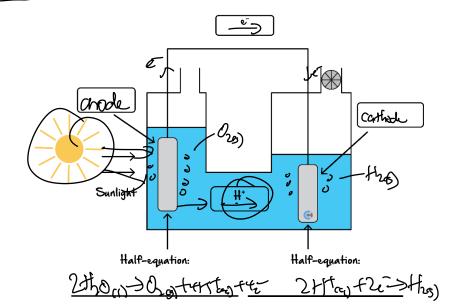
Now, let's have a look at another 'green' production method of hydrogen gas!



- Electrolysis of Acidic Water:
  - Half-Equations:



- 6 Overall Equation: 24hours Ozor +24hours
- > 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: Solar > Chemica).
- 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]
  - Guse of renewable feedstocks: [Relevant] / [Not Relevant]

# How does the solar energy cause electrolysis?



Protons

Molecular Formula:

# **Exploration**: Natural Photosynthesis



Reaction:

$$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g)$$

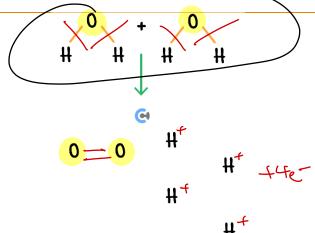
Energy Used: \_\_Cold

# Two Stages

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



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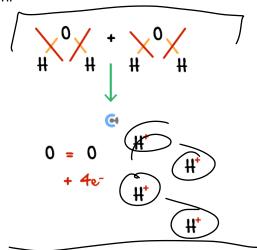


- Half-Reaction:
- > Stage #2 Light-independent stage Protons are combined with carbon dioxide to produce glucose.

# 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:



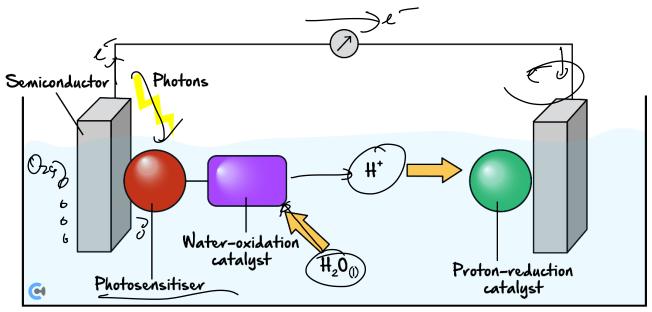
- **G** Half-Reaction:  $2H_2O(1) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
- @ Catalyst: wake-oxdidution catalyst

# **ONTOUREDUCATION**

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- > Stage #2: Light-independent stage Protons are converted to \_\_\_\_\_\_ molecules
  - G Structural Formula Reaction:

- Half-Reaction: 2447200
- @ Catalyst: profon-reduction contralyst
- Possible Setup #1:



Oxidation:

$$2H_2O_{(1)} \rightarrow O_{2(q)} + 4H^+_{(aq)} + 4e^-$$

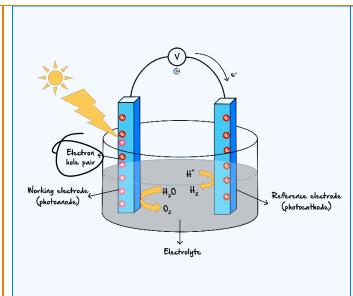
$$2 \underline{\text{H}^+_{(aq)}} + 2 e^- \rightarrow \underline{\text{H}_{2(q)}}$$

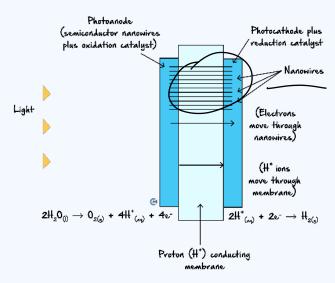
- > Water-oxidation catalyst & Proton-reduction catalyst issues:
- Possible Setups #2 & #3:

# Possible Setup #2:

Possible Setup #3:





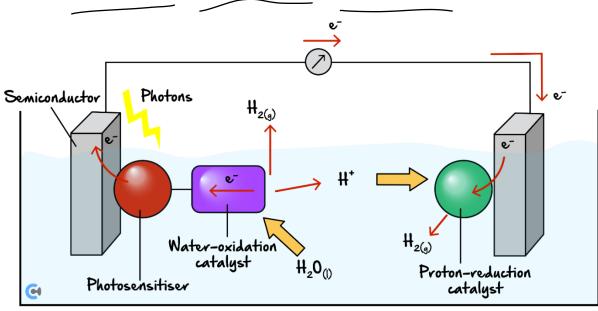


# Definition

#### **Artificial Photosynthesis Cell**

Artificial Photosynthesis Alternative Name:

# "water oxidation and proton reduction catalyst system"



Oxidation:

Reduction:

$$2H_{2}O_{(j)} \to O_{2(g)} + 4H^{^{+}}{}_{(aq)} + 4e^{-}$$

$$2\textnormal{H}^{^{+}}{}_{(\textrm{\tiny aq})} + 2\textnormal{\tiny e}^{\text{\tiny -}} \rightarrow \textnormal{H}_{2(\textrm{\tiny q})}$$

- ► Energy Conversion: <u>Solv</u> → Chem
- Energy Efficiency: [High] / [Low]



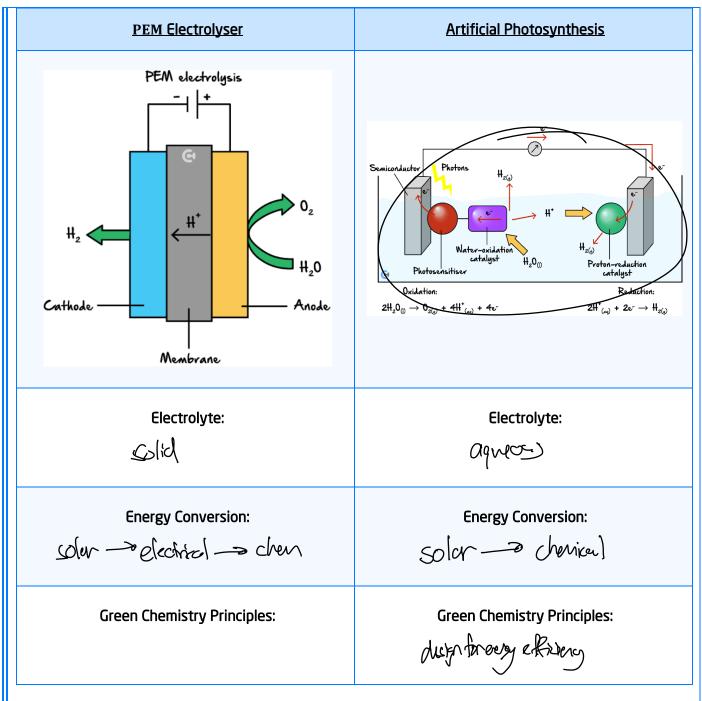
#### PEM Electrolyser vs Artificial Photosynthesis Cell

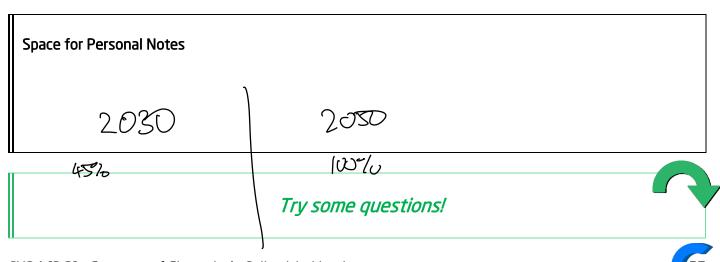
# Similarities:

- Reaction: Electrolysis of <u>aidに walv</u>
  - $\bigcirc$  Cathode:  $2H^+ + 2e^- \rightarrow H_2$
  - Anode:  $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
- Energy Used: Solar (PEM: Wind)
- United Nations Sustainable Development Goals:
  - 1. Goal 7: Affordable Lofon Clanter for offindable
  - z. Goal 13: Climak action \_ solur/viral-prenewable
  - 3. Goal 6: Clean water & santeitien -
    - > water supply: large amounts of water required.
      > water purity earlier: requires ones
- Green chemistry principles: (Cotal 45)
- Disadvantages:

Differences:









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)

water oxidises according to following:

2+120 -> 02 + 4+1+4e-

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

protons are Ht ions which reduce

2+1+ 2e-> +2
(ca)

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

oxygen gas

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

direct every conv from salar -> chem

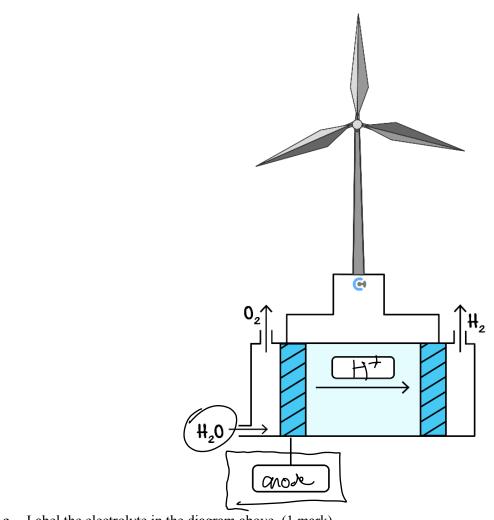
c. Using two relevant sustainable development goals, state two major challenges associated with the widespread use of artificial photosynthesis to produce hydrogen gas on a larger scale. Use item (26) (i) of the Data Book. (2 marks)

h	Using a relevant sustainable development goal, state <b>one</b> major environmental benefit that this process could ave if it is adopted on a large scale. Use <b>item (26) (i)</b> of the Data Book. (1 mark)  Goal 13 - climate action - as it uses solar energy which is renewable form of energy.

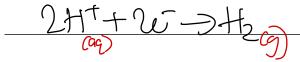
Question 19 (4 marks)

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

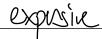




- **a.** Label the electrolyte in the diagram above. (1 mark)
- b.
- i. Label the left electrode as the cathode or anode in the box provided above. (1 mark)
- ii. Write the half-reaction which occurs at the negative electrode. (1 mark)



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



# **Contour Check**





□ <u>Learning Objective</u>: [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.
  - O Sodium ions are concentrations greater than 4.0 *M* concentration [react] / [do not] react in preference to water.

Learning Objective: [2.2.2] - Identify features

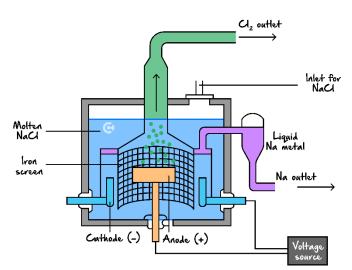


# of electrolytic cells & their purpose

#### 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:	react species wealer than wah
Iron at the cathode:	react species weaker than water carthode weaker anyway
Other Electrolytes (e.g., CaCl <sub>2</sub> ) added:	reduce melting point.
Barrier within the cell:	<b>G</b> ,
· products don't spon rec	activa direct contact
· allows ions to pass the	rough.
Products constantly removed:	O
o don't react	·
· merfecul cell	·

□ Enclosed container: Oz doent interfere

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**

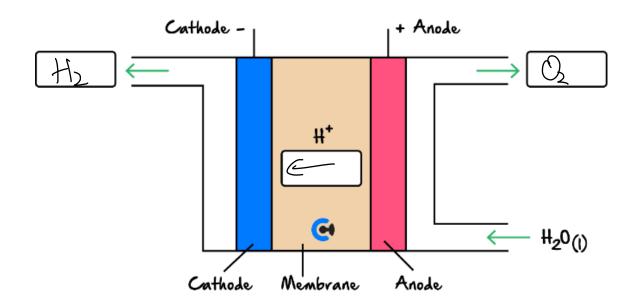
"the role of innovation in designing cells to meet society's energy needs in terms of producing 'green' hydrogen (including equations in acidic conditions) using the following methods:

- 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 Cardia waw.
- PEM Electrolyser:

# PEM electrolysis



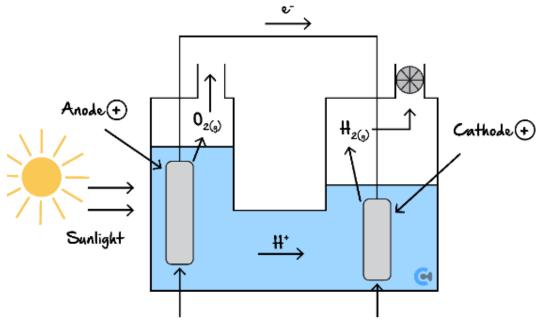
<u>Cathode</u> <u>Anode</u>



2Ht ag + 2e-> H20)

24200 - Org +44+4-

- O Energy Used: Slaviuind
- O Green Chemistry Principle: Catalusis
- Artificial Photosynthesis:



Half-equation:

Half-equation:

$$H_2O_{(i)} \rightarrow O_{2(j)} + 4H^*_{(nq)} + 4e^- \qquad 2H^*_{(nq)} + 2e^- \rightarrow H_{2(j)}$$

- Energy Conversion: Solar → Chem
- Green Chemistry Principle: design for everyoff / ratalyst



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