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VCE Chemistry $\frac{3}{4}$
Introduction to Electrolysis [2.1]
Workbook

Outline:



Non-Spontaneous Redox Reactions

Pg 2-5

Electrolysis

Pg 6-20

- Introduction to Electrolytic Cells
- Electrolytic Cell
- Electrolysis of Water

Predicting Electrolytic Reactions

Pg 21-46

- Predicting Electrolytic Reactions
- Unique Species on the Electrochemical Series
- Observations in Electrolytic Cells
- Electrolytic Cells Electrodes
- Input of Voltage

Learning Objectives:

- ❑ CH34 [2.1.1] - Identify Differences Between Galvanic & Electrolysis for Electrodes, Energy Conversions, Electron Flow
- ❑ CH34 [2.1.2] - Write Equations & Calculate EMF Required for Electrolytic Reactions



Section A: Non-Spontaneous Redox Reactions

So far, only the spontaneous redox reactions have been considered.

Let's take a look at non-spontaneous redox reactions.

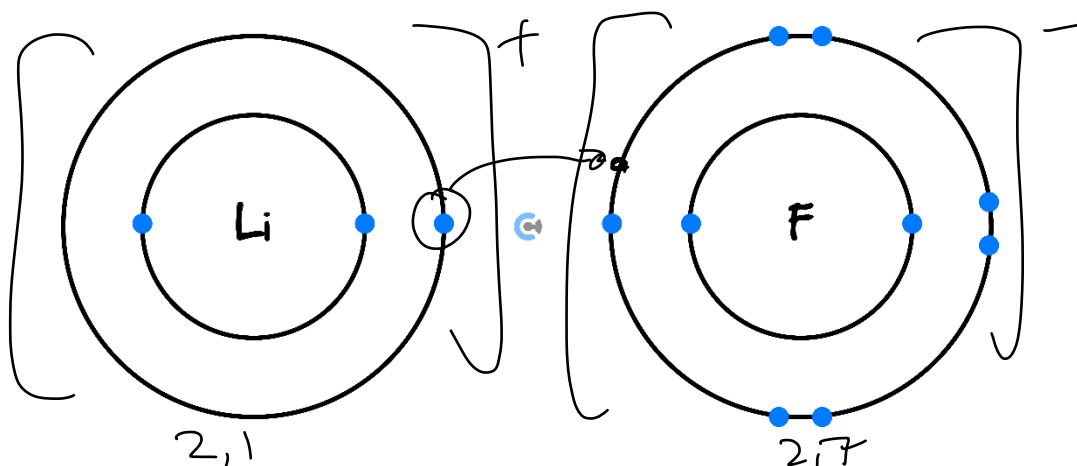
Active Recall: What is a spontaneous reaction?

occurs by itself w/o required input of energy

Exploration: Lithium Fluoride (LiF)

➤ Consider two substances, Lithium (Li) and Fluorine (F):

🔗 How will the bonding look like between them? *(Label Below)*

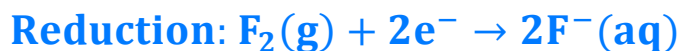


🔗 Type of Intramolecular Bonding: [Ionic] / [Covalent] / [Metallic]

➤ Lithium (Li) and Fluorine (F):

Lithium (Li)	Fluorine (F)
[gained] / [lost] electrons	[gained] / [lost] electrons
[reduction] / [oxidation] half-equation	[reduction] / [oxidation] half-equation

➤ Half-Reactions:



➤ Bonding: [occurs by itself] / [forced]

Let's consider oxidant/reductant strengths properly!

Exploration: Oxidant/Reductant Strength of Li(s) & $\text{F}_2(\text{g})$

➤ Find the location of both the **Lithium (Li)** and the **Fluorine gas (F_2)**:

Reaction	Standard electrode potential (E^\ominus) in volts at 25 °C
$\text{F}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{F}^-(\text{aq})$	+2.87
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O(l)}$	+1.77
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O(l)}$	+1.51
$\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{H}_2\text{O(l)}$	+1.47
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O(l)}$	+1.36
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$	+1.36
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O(l)}$	+1.23
$\text{Br}_2(\text{l}) + 2\text{e}^- \rightleftharpoons 2\text{Br}^-(\text{aq})$	+1.09
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag(s)}$	+0.80
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn(s)}$	-0.76
$2\text{H}_2\text{O(l)} + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Mn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Mn(s)}$	-1.18
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Al(s)}$	-1.66
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Mg(s)}$	-2.37
$\text{Na}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Na(s)}$	-2.71
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ca(s)}$	-2.87
$\text{K}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{K(s)}$	-2.93
$\text{Li}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Li(s)}$	-3.04

➤ Reactants:

Lithium (Li(s))	Fluorine Gas ($\text{F}_2(\text{g})$)
[strong] / [weak] - [oxidant] / [reductant]	[strong] / [weak] - [oxidant] / [reductant]

➤ Type of Reaction: spontaneous reaction occurs.

➤ Energy: [energy used] / [energy released] Chem → therm

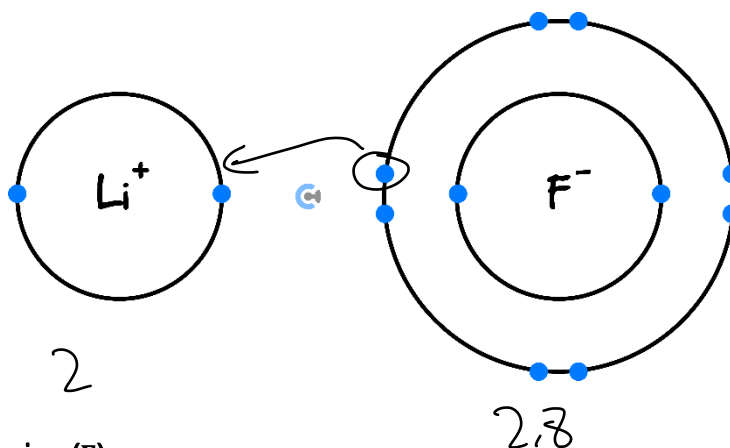
How About the Opposite Reaction?

Exploration: Oxidant/Reductant Strength of Li(s) & $\text{F}_2(\text{g})$

➤ Consider the products of this reaction, the $\text{Li}^+(\text{aq})$ and $\text{F}^-(\text{aq})$.

When Going Backwards...

➤ What will the bonding look like between them? (*Label Below*)



➤ Lithium (Li) and Fluorine (F):

Lithium Ion ($\text{Li}^+(\text{aq})$)	Fluoride Ion ($\text{F}^-(\text{aq})$)
[gained] / [lost] electrons	[gained] / [lost] electrons
[reduction] / [oxidation] half-equation	[reduction] / [oxidation] half-equation

➤ Half-Reactions:



- Will this naturally occur? [Yes] / [No]
- Breaking of Bonding: [occurs by itself] / [forced]
- To Force Reaction, Energy is: [inputted] / [released]
- On the Electrochemical Series:

Lithium Ion ($\text{Li}^+(\text{aq})$)	Fluoride Ion ($\text{F}^-(\text{aq})$)
[strong] / [weak] - [oxidant] / [reductant]	[strong] / [weak] - [oxidant] / [reductant]

Discussion: What type of energy must be inputted for this reaction to occur? (Hint: We need to move electrons)



electric

Terminology

- **Electrical Energy** is Inputted to **Break Down** $\text{LiF}(\text{aq})$.

➤ Terminology:

Electrolysis

- ⚙ 'electro-': using electricity
- ⚙ '-lysis': to separate or break.



Section B: Electrolysis

Sub-Section: Introduction to Electrolytic Cells

Let's have a look at what the actual cells look like!

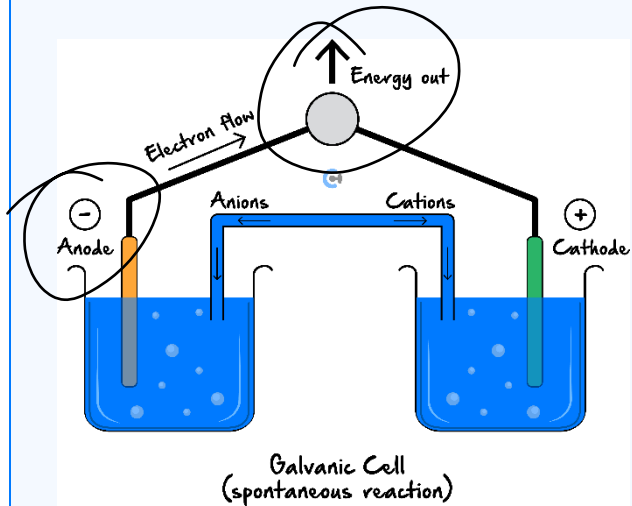
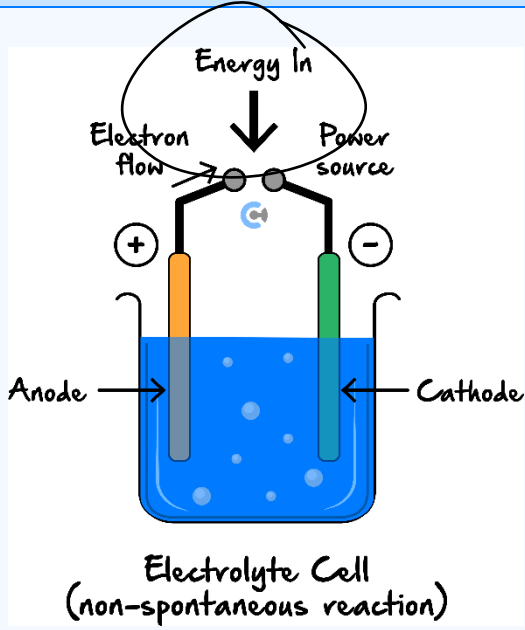
Electrolysis

- **Definition:** Input of electrical energy is to force a non-spontaneous reaction to occur.
- **Electron Movement:** fore electrons in opposite direction.
- Process is electrolysis. Cells are: Electrolytic cell
- **Comparison:**

Galvanic Cell	Electrolytic Cell
Spontaneous Redox Reaction	Non-spontaneous Redox Reaction
<p>Produces electrical energy.</p> <p>Chemical → Electrical</p>	<p>Consumes electrical energy.</p> <p>Electrical → Chemical</p>

Let's first compare the differences between galvanic and electrolytic cells!

Discussion: What are some differences between the galvanic cell and electrolytic cell?

Galvanic Cell	Electrolytic Cell
 <p>Galvanic Cell (spontaneous reaction)</p>	 <p>Electrolytic Cell (non-spontaneous reaction)</p>
<p>Anode \ominus Cathode \oplus</p> <p>AO \ominus RC \oplus</p>	<p>AO \oplus RC \ominus</p>
<p>separated half-cells</p>	<p>shared electrolyte no salt bridge</p>
<p>produce energy</p>	<p>uses energy</p>

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Why can electrolysis share an electrolyte?

Exploration: Sharing Electrolyte

What happens when both reactants are put in the same electrolyte?

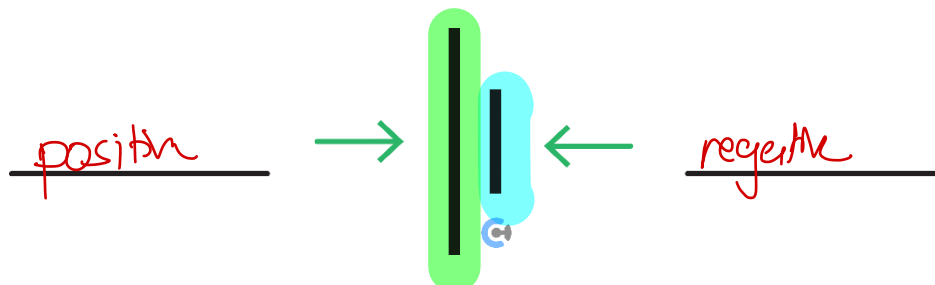
Galvanic Cell	Electrolytic Cell
<p>Galvanic Cell (spontaneous reaction)</p> <p>$Zn \mid Cu^{2+}$</p> <p>Chem \rightarrow therm</p>	<p>Electrolyte Cell (non-spontaneous reaction)</p> <p>no reaction</p>

- **Conclusion:** Electrolysis can share an electrolyte because reactants [will] / [will not] react when placed together.

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Before we look at an electrolytic cell in depth, let's recap a few things!

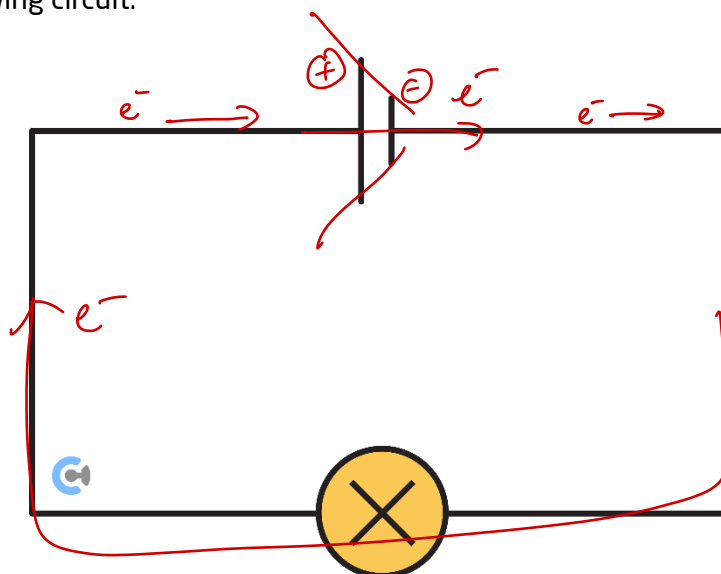
Active Recall: Which side was positive and negative of a cell?



How do electrons flow?

Exploration: Electron Flow

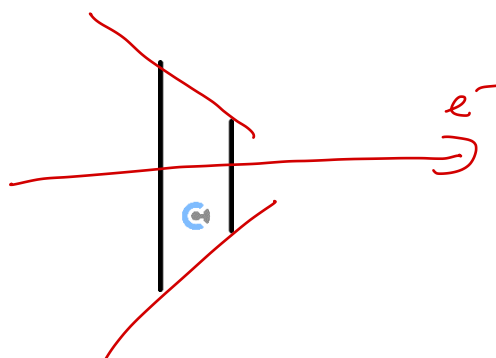
➤ Consider the following circuit:



- 🔊 Where are the positive and negative terminals of the cell? *(Label Above)*
- 🔊 Imagine an electron to the right of the cell. How will it move in reference to this negative terminal of the battery? [attracted] / [repelled]
- 🔊 Which way do the electrons flow? *(Label Below)*



TIP: The electron flow and thus the anode/cathode is determined by the direction of electron flow. The battery can be visualised as a **funnel** for the electrons:



Active Recall: What type of reaction occurs at each electrode?



Cathode	Anode
reduction	oxidation

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Sub-Section: Electrolytic Cell

Exploration: Electrolytic Cell

➤ Consider the electrolysis of lithium fluoride (LiF).

➤ Half-Equations:

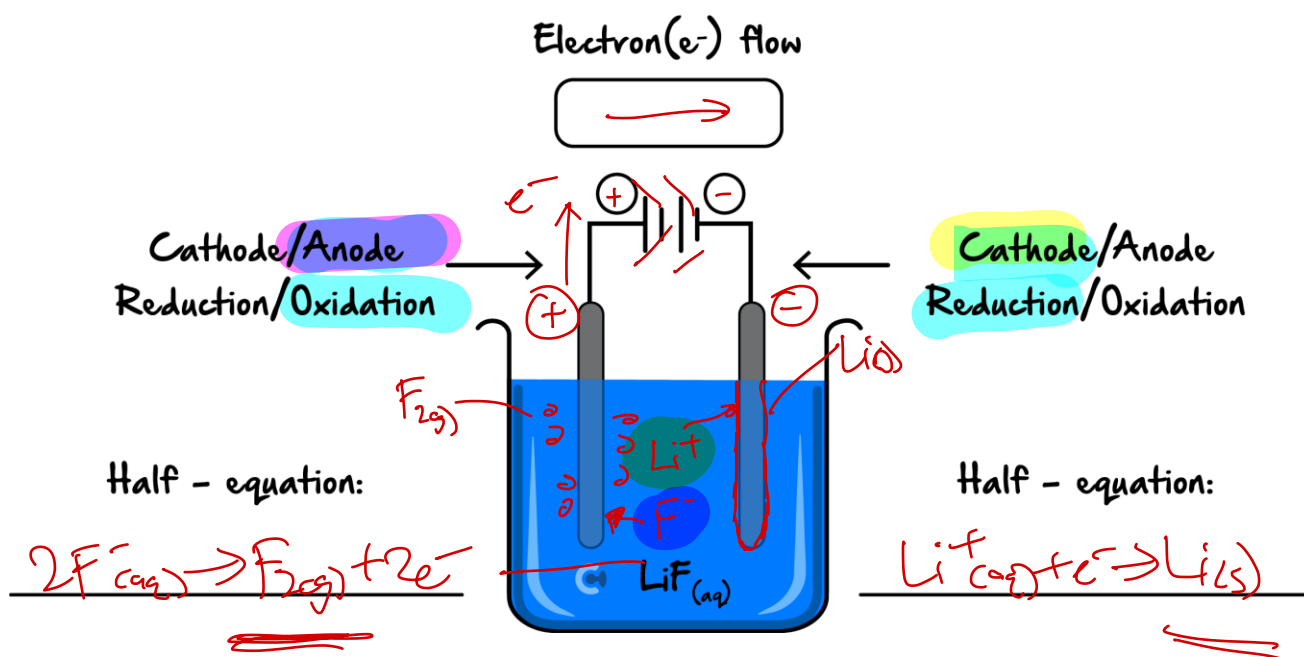


➤ Electrolytic Cell Labelled:

⚙ What happens at the left and right electrode? How about the half-equations? (Label Below)

⚙ Which way do electrons flow? (Label Below)

⚙ How will reactants move to form products? (Label Below)



➤ Considering the Ions & Electrolyte Movement:

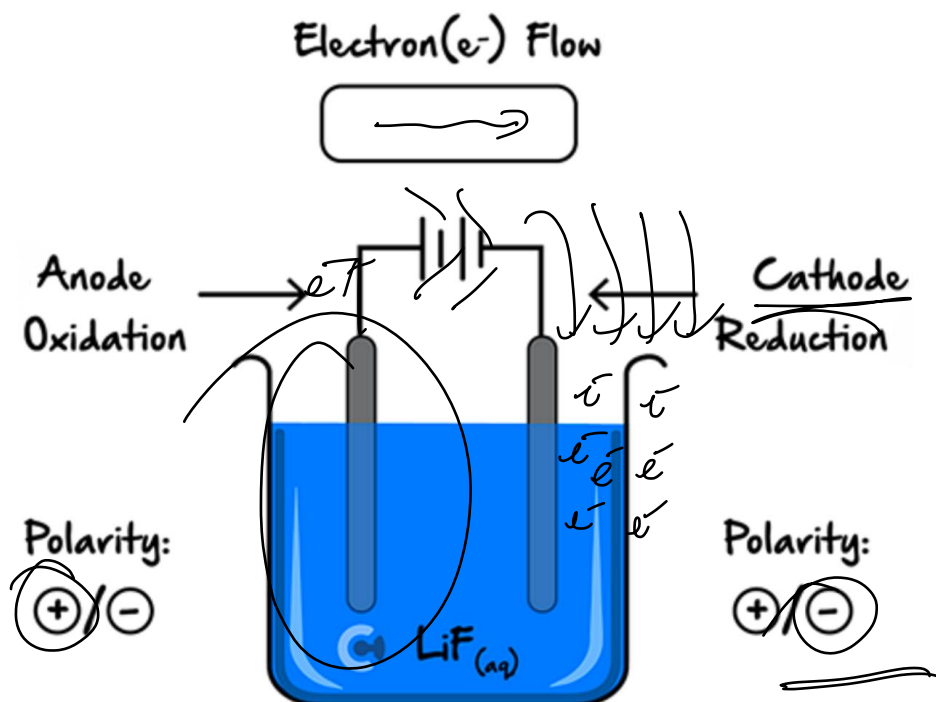
Lithium Ions ($\text{Li}^+(\text{aq})$)	Fluoride Ions ($\text{F}^-(\text{aq})$)
[cation] / [anion]	[cation] / [anion]
Moves towards [cathode] / [anode]	Moves towards [cathode] / [anode]

➤ The movement of electrolytes maintain electric neutrality.

➤ Salt Bridge for Electrolysis: [required] / [not required]

Exploration: Polarities of Electrodes

➤ Consider the following Electrolytic Cell:



⚙ Polarity of Batteries & Electron Movement: (Label Above)

⚙ Half-Equation Type & Cathode/Anode: (Label Above)

⚙ As electrons arrive at the cathode, charge at the cathode: more [positive] / [negative]

⚙ Polarity of Electrodes: (Label Above)

Why is this the case?

➤ Electron flow is always anode to cathode.

Galvanic Cells	Electrolytic Cells
Polarity is imposed by the reactions themselves.	Polarity is imposed by the power source.
[Spontaneous] / [Non-Spontaneous] Reaction	[Spontaneous] / [Non-Spontaneous] Reaction
Reaction is [natural] / [forced]	Reaction is [natural] / [forced]

TIP: You can think of electrons as slaves.



Electrode Polarities

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AOP

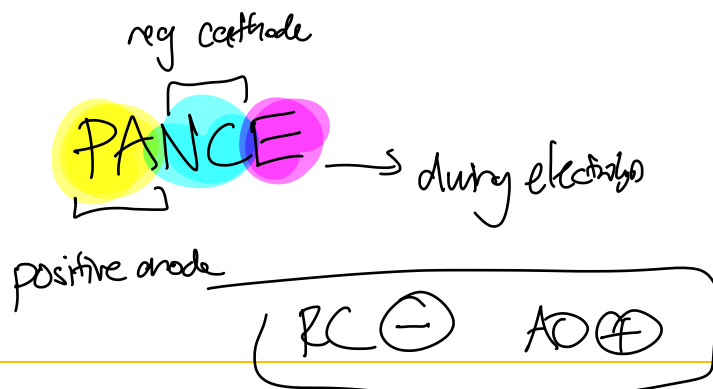
Cathode	Anode
[reduction] / [oxidation]	[reduction] / [oxidation]
[positive] / [negative] electrode	[positive] / [negative] electrode



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TIP: How can we remember this?



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Sub-Section: Electrolysis of Water

Let's have a look at what happens during the electrolysis of water!

To do so, let's first find water on the electrochemical series!

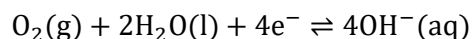
Exploration: Water Equations on the Electrochemical Series

- Where is water on the electrochemical series (ECS)? *(Circle Below)*.

Reaction	Standard electrode potential (E^0) in volts at 25 °C
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.77
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$PbO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O(l)$	+1.47
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.36
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+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
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.68
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	+0.15
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	-0.13
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	-0.14
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	-0.25
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	-0.28
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	-0.76
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	-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
$K^+(aq) + e^- \rightleftharpoons K(s)$	-2.93
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	-3.04

- What/where is the strongest oxidant and strongest reductant forms of water? (*Label Above*)

NOTE: The water half-equation at an $E^\circ = +0.40\text{ V}$ needs oxygen gas to react, which is not always present, so we do not use this equation if we only have water!



ALSO NOTE: This half-equation is the reduction of oxygen in an alkaline fuel cell!



Water Electrolysis



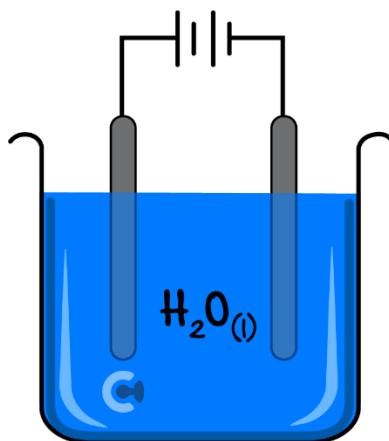
- Water Reduction Half-Equation: $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$
- Water Oxidation Half-Equation: $2\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$

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Let's go through a question together!

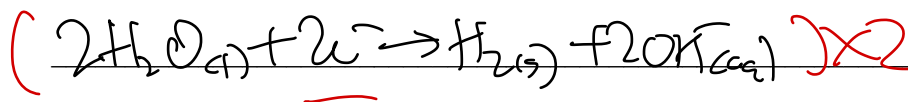
Question 1 Walkthrough.

Electricity is run through some water according to the following setup.

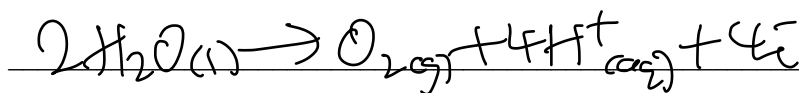


a. Write the balanced half-equation for the:

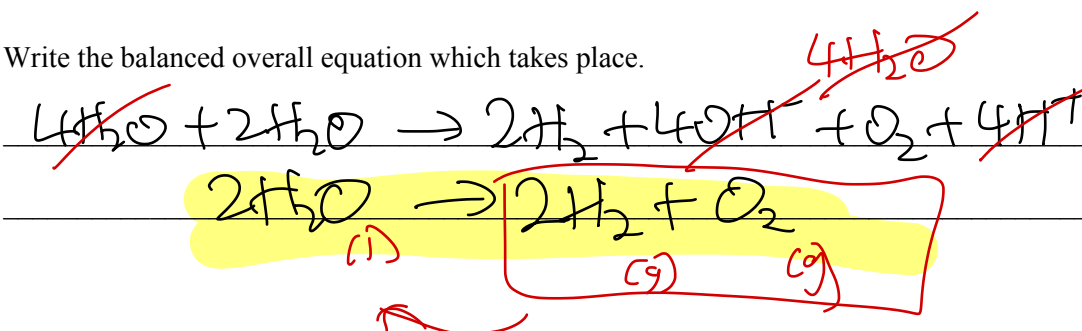
i. Reduction half-equation.



ii. Oxidation half-equation.



b. Write the balanced overall equation which takes place.

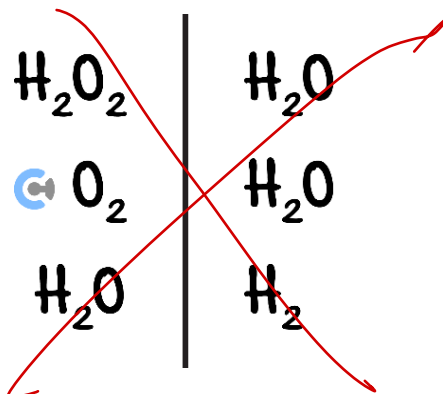


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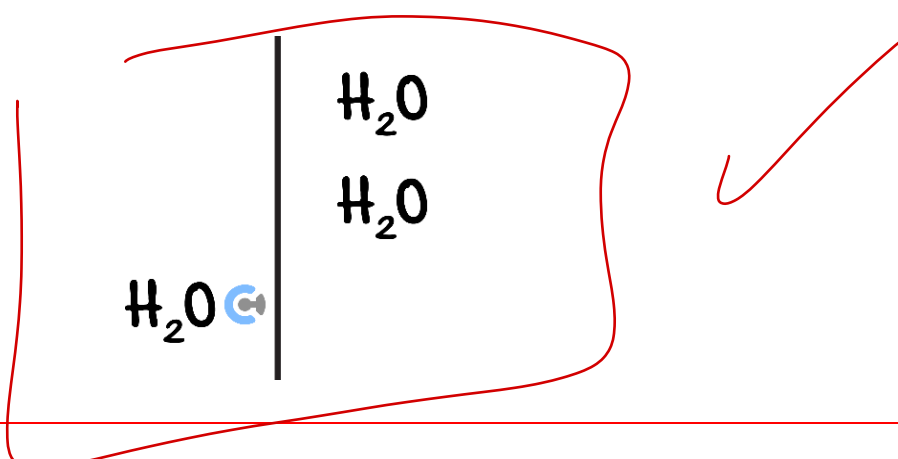
Misconception

"During the Electrolysis of Water, hydrogen peroxide will react with hydrogen gas as the strongest oxidant reacts with the strongest reductant."



TRUTH:

When constructing the electrochemical series, only include what species is present!



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Where has this reaction been seen before?



Comparison of Spontaneous vs Non-Spontaneous Reactions



Reaction	$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$	$2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$
Type of Reaction	combustion H_2	Electrolysis of water
Spontaneity	[spontaneous] / [non-spontaneous]	[spontaneous] / [non-spontaneous]
Endothermic/Exothermic	[endothermic] / [exothermic]	[endothermic] / [exothermic]
Energy	[uses] / [produces] energy	[uses] / [produces] energy
Energy Conversions	chem \rightarrow thermal/elec	elec \rightarrow chemical

Recall!



Active Recall: How do the electrodes look like in an electrolytic cell?



Electrode	Cathode	Anode
Type of Half-Reaction	[reduction] / [oxidation]	[reduction] / [oxidation]
Polarity	[positive] / [negative]	[positive] / [negative]

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Question 2

At the anode of an electrolytic cell:

- A. Reduction occurs and its polarity is positive.
- B. Oxidation occurs and its polarity is positive.
- C. Reduction occurs and its polarity is negative.
- D. Oxidation occurs and its polarity is negative.



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Section C: Predicting Electrolytic Reactions

Sub-Section: Predicting Electrolytic Reactions

Let's now try to predict equations that will occur in Electrolytic Reactions!

Predicting Electrolytic Reaction Steps

1. Identify all species present (check if water is present)!
2. Draw Vertical Line.
3. The strongest oxidant will always react with the strongest reductant.
 -  Strongest oxidant is the oxidant (left side of the ECS) which is highest up.
 -  Strongest reductant is the reductant (right side of the ECS) which is lowest down.
4. Identify the reactions which will take place and note them down.

<u>Electrode</u>	<u>Cathode</u>	<u>Anode</u>
Type of Half-Reaction	[reduction] / [oxidation]	[reduction] / [oxidation]
Polarity	[positive] / [negative]	[positive] / [negative]

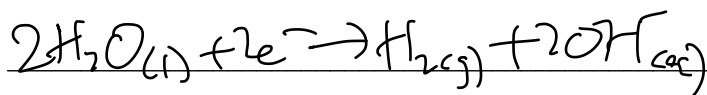
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Let's have a look at a question together!

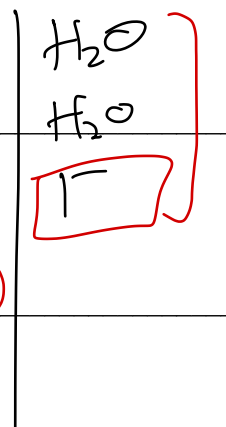
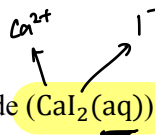
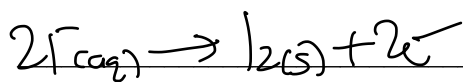
Question 3 Walkthrough.

Write the equations which take place when a solution of calcium iodide ($\text{CaI}_2(\text{aq})$) is electrolysed using inert electrodes.

a. Reduction half-equation.



b. Oxidation half-equation.



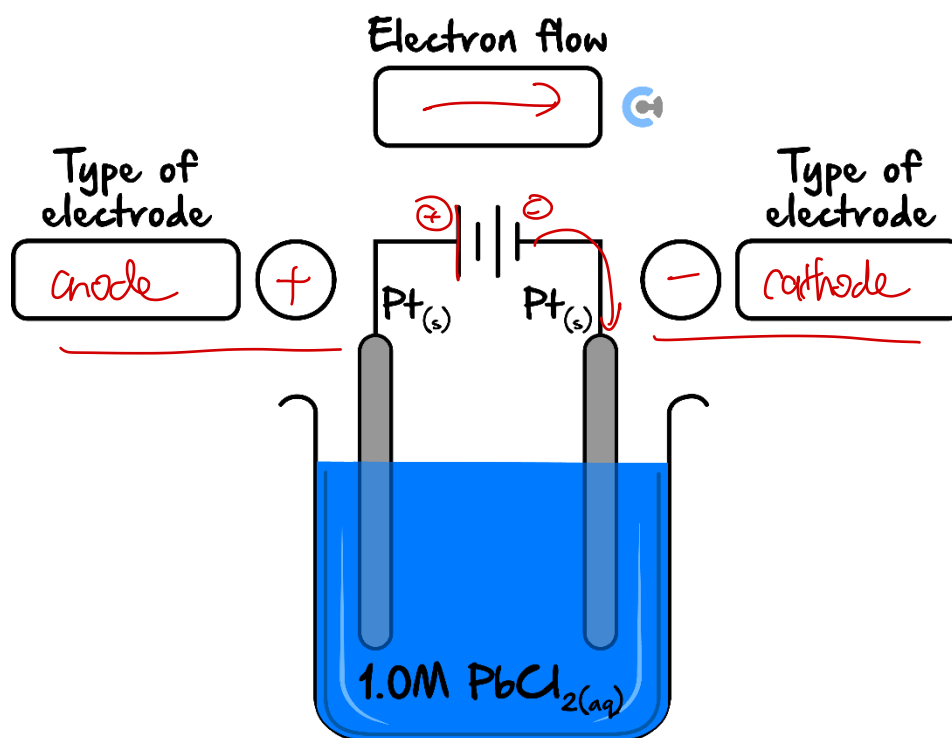
NOTE: H_2O needs to be considered as it will sometimes be the strongest oxidant/reductant.

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Let's have a look at another question together!

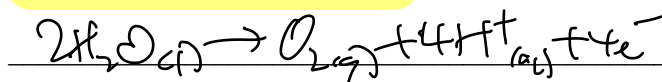
Question 4 Walkthrough.

Consider an electrolytic cell involving the electrolysis of $\text{PbCl}_2(\text{aq})$ solution using platinum electrodes, as shown below.

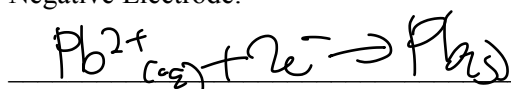


- Label the type of electrode as cathode or anode for each electrode, along with their polarities in the relevant circles provided above.
- Label the direction of electron flow in the diagram provided above.
- Write the half-equations which occur at the:

i. Positive Electrode. AO



ii. Negative Electrode.



NOTE: Don't forget $\text{Pb(s)} + \text{H}_2\text{O(l)}$ is on the ECS as well!



Extension: Why hasn't water needed to be considered in galvanic cells as a potential oxidant/reductant?

- Water has **always** been present!
- Find Water in Both Scenarios.
- Likelihood of Water Reacting:

Galvanic	Electrolytic																																																																																																																												
$\text{Cl}_2(\text{g})$ reacting with Zn(s)	$\text{Cl}^-(\text{aq})$ reacting with $\text{Zn}^{2+}(\text{aq})$																																																																																																																												
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4\text{H}^+(\text{aq}) + 4\text{e}^- = 2\text{H}_2\text{O(l)}$	+1.23	$\text{Br}_2(\text{l}) + 2\text{e}^- = 2\text{Br}^-(\text{aq})$	+1.09	$\text{Ag}^+(\text{aq}) + \text{e}^- = \text{Ag(s)}$	+0.80	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- = \text{Fe}^{2+}(\text{aq})$	+0.77	$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- = \text{H}_2\text{O}_2(\text{aq})$	+0.68	$\text{I}_2(\text{s}) + 2\text{e}^- = 2\text{I}^-(\text{aq})$	+0.54	$\text{O}_2(\text{g}) + 2\text{H}_2\text{O(l)} + 4\text{e}^- = 4\text{OH}^-(\text{aq})$	+0.40	$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- = \text{Cu(s)}$	+0.34	$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- = \text{Sn}^{2+}(\text{aq})$	+0.15	$2\text{H}^+(\text{aq}) + 2\text{e}^- = \text{H}_2(\text{g})$	0.00	$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- = \text{Pb(s)}$	-0.13	$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- = \text{Sn(s)}$	-0.14	$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- = \text{Ni(s)}$	-0.25	$\text{Co}^{2+}(\text{aq}) + 2\text{e}^- = 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2\text{F}^-(\text{aq})$	+2.87	$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- = 2\text{H}_2\text{O(l)}$	+1.77	$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- = \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O(l)}$	+1.51	$\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- = \text{Pb}^{2+}(\text{aq}) + 2\text{H}_2\text{O(l)}$	+1.47	$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- = 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O(l)}$	+1.36	$\text{Cl}_2(\text{g}) + 2\text{e}^- = 2\text{Cl}^-(\text{aq})$	+1.36	$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- = 2\text{H}_2\text{O(l)}$	+1.23	$\text{Br}_2(\text{l}) + 2\text{e}^- = 2\text{Br}^-(\text{aq})$	+1.09	$\text{Ag}^+(\text{aq}) + \text{e}^- = \text{Ag(s)}$	+0.80	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- = \text{Fe}^{2+}(\text{aq})$	+0.77	$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- = 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\text{Al(s)}$	-1.66	$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- = \text{Mg(s)}$	-2.37	$\text{Na}^+(\text{aq}) + \text{e}^- = \text{Na(s)}$	-2.71	$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- = \text{Ca(s)}$	-2.87	$\text{K}^+(\text{aq}) + \text{e}^- = \text{K(s)}$	-2.93	$\text{Li}^+(\text{aq}) + \text{e}^- = \text{Li(s)}$	-3.04
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$\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- = \text{Pb}^{2+}(\text{aq}) + 2\text{H}_2\text{O(l)}$	+1.47																																																																																																																												
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- = 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O(l)}$	+1.36																																																																																																																												
$\text{Cl}_2(\text{g}) + 2\text{e}^- = 2\text{Cl}^-(\text{aq})$	+1.36																																																																																																																												
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- = 2\text{H}_2\text{O(l)}$	+1.23																																																																																																																												
$\text{Br}_2(\text{l}) + 2\text{e}^- = 2\text{Br}^-(\text{aq})$	+1.09																																																																																																																												
$\text{Ag}^+(\text{aq}) + \text{e}^- = \text{Ag(s)}$	+0.80																																																																																																																												
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- = \text{Fe}^{2+}(\text{aq})$	+0.77																																																																																																																												
$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- = \text{H}_2\text{O}_2(\text{aq})$	+0.68																																																																																																																												
$\text{I}_2(\text{s}) + 2\text{e}^- = 2\text{I}^-(\text{aq})$	+0.54																																																																																																																												
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O(l)} + 4\text{e}^- = 4\text{OH}^-(\text{aq})$	+0.40																																																																																																																												
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- = \text{Cu(s)}$	+0.34																																																																																																																												
$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- = \text{Sn}^{2+}(\text{aq})$	+0.15																																																																																																																												
$2\text{H}^+(\text{aq}) + 2\text{e}^- = \text{H}_2(\text{g})$	0.00																																																																																																																												
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- = \text{Pb(s)}$	-0.13																																																																																																																												
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- = \text{Sn(s)}$	-0.14																																																																																																																												
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- = \text{Ni(s)}$	-0.25																																																																																																																												
$\text{Co}^{2+}(\text{aq}) + 2\text{e}^- = \text{Co(s)}$	-0.28																																																																																																																												
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- = \text{Fe(s)}$	-0.44																																																																																																																												
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- = \text{Zn(s)}$	-0.76																																																																																																																												
$2\text{H}_2\text{O(l)} + 2\text{e}^- = \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83																																																																																																																												
$\text{Mn}^{2+}(\text{aq}) + 2\text{e}^- = \text{Mn(s)}$	-1.18																																																																																																																												
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- = \text{Al(s)}$	-1.66																																																																																																																												
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- = \text{Mg(s)}$	-2.37																																																																																																																												
$\text{Na}^+(\text{aq}) + \text{e}^- = \text{Na(s)}$	-2.71																																																																																																																												
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- = \text{Ca(s)}$	-2.87																																																																																																																												
$\text{K}^+(\text{aq}) + \text{e}^- = \text{K(s)}$	-2.93																																																																																																																												
$\text{Li}^+(\text{aq}) + \text{e}^- = \text{Li(s)}$	-3.04																																																																																																																												
Water is so much <u>weaker</u> than the reactants.	Water is <u>similar</u> in strength to the reactants, and reacts in preference to the $\text{Cl}^-(\text{aq})$.																																																																																																																												

REMINDER: Water is always present in solutions!



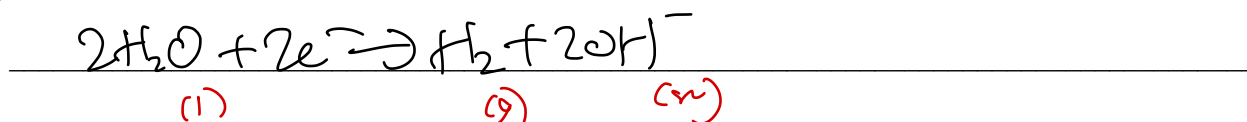
Your Turn!



Question 5

What are the expected electrolytic products of the electrolysis of magnesium iodide $\text{MgI}_2(\text{aq})$ solution? Write the half-equations occurring at both the anode and cathode.

a. Cathode reaction:



b. Anode reaction:



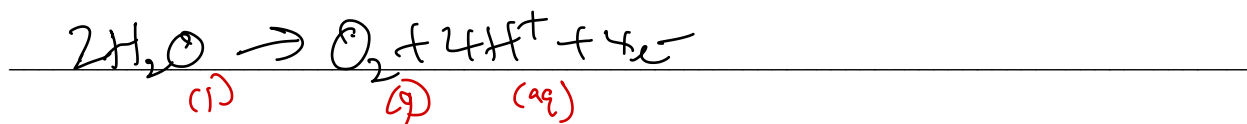
Question 6

What are the expected electrolytic products of the electrolysis of copper fluoride $\text{CuF}_2(\text{aq})$ solution? Write the half-equations occurring at both the anode and cathode.

a. Cathode reaction:



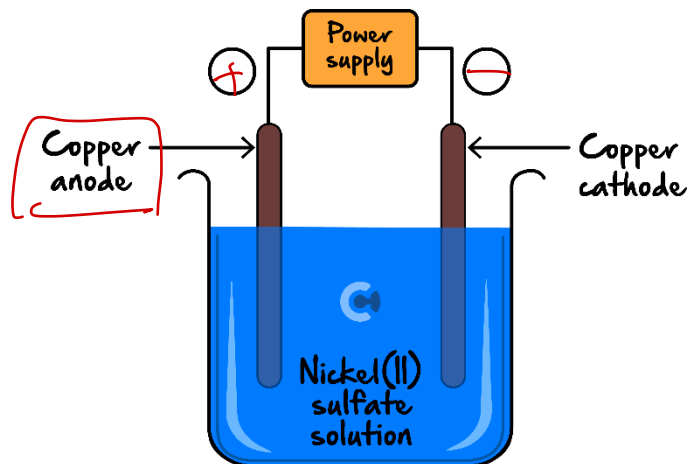
b. Anode reaction:



Space for Personal Notes

Question 7

The electrolysis of 1 M nickel (II) sulphate solution is undertaken with copper (Cu(s)) electrodes at 25°C. A diagram of this electrolytic process is shown in the following figure:



a. Label the polarity of each electrode in the diagram above.

b. Write the half-equations which occur at the:

i. Cathode.



ii. Anode.

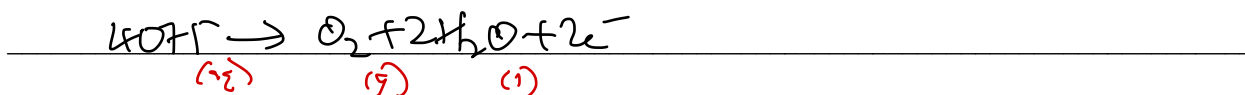


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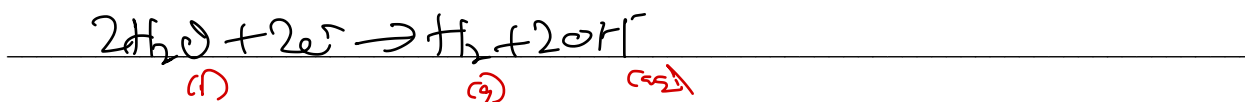
Question 8 Additional Question.

Write the half-equations which occur when a solution of sodium hydroxide is electrolysed.

a. Positive electrode half-equation.



b. Negative electrode half-equation.



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Sub-Section: Unique Species on the Electrochemical Series



Just like in galvanic cells, there are two metal ions which appear twice on the electrochemical series.



Active Recall: What were the two metal ions which appear twice on the electrochemical series?



- Fe²⁺
- Sn²⁺

REMINDER: There are two ways to determine charges on ions:



- **Roman Numerals** - Iron (II) nitrate vs Iron (III) nitrate
- **Ionic Compound** - Fe(NO₃)₂ vs Fe(NO₃)₃

Space for Personal Notes

Let's look at a question together!

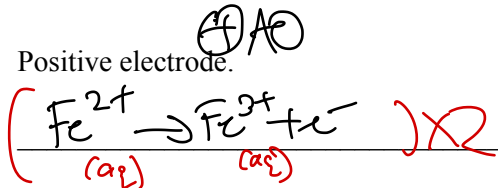


Question 9 Walkthrough.

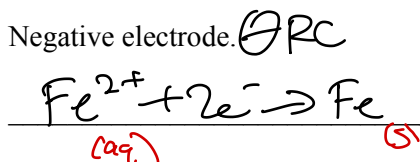
A solution containing iron (II) nitrate is electrolysed using inert electrodes.

a. Predict the reactions which occur at the:

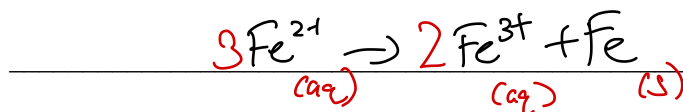
i. Positive electrode.



ii. Negative electrode.



b. Write the overall reaction which takes place.

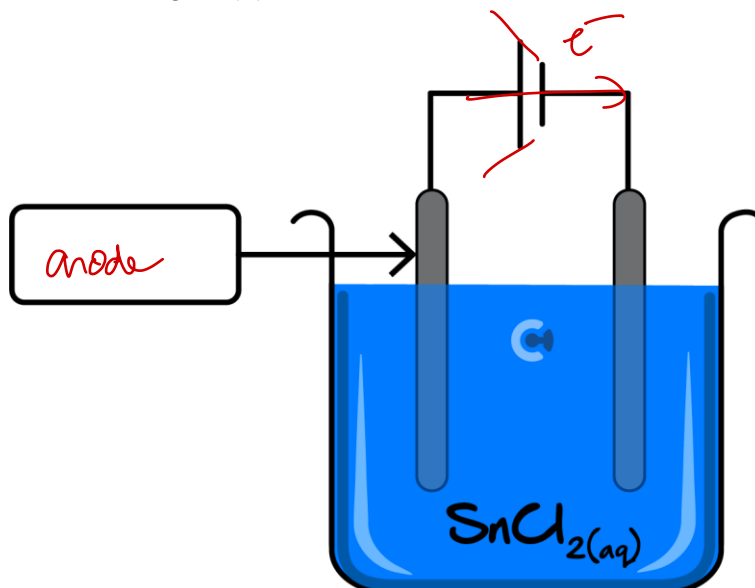


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Your Turn!

Question 10

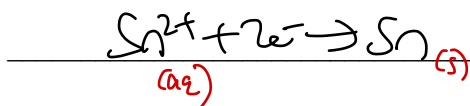
The electrolysis of a solution containing tin (II) chloride is undertaken. Inert electrodes were used.



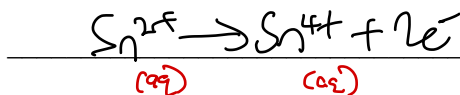
In the box provided above, label the left electrode as being the cathode or anode.

a. Write the balanced half-equations for the:

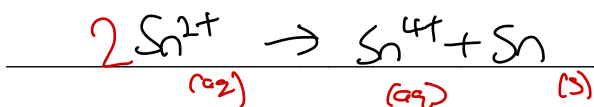
i. Reduction reaction.



ii. Oxidation reaction.



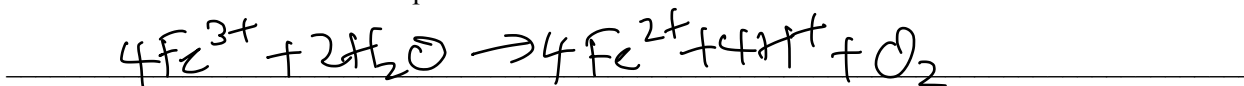
b. Write the overall reaction which takes place.



Question 11 Additional Question.

A solution of iron (III) fluoride is electrolysed using inert electrodes.

Write the overall reaction which takes place.



Space for Personal Notes

Sub-Section: Observations in Electrolytic Cells



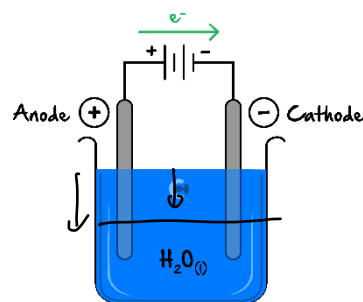
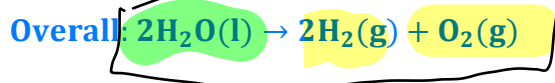
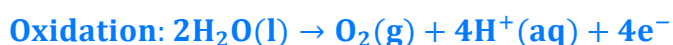
Context

- Just like in galvanic cells, observations can be made in electrolytic cells.
- ⚙ Change in **mass/size** of the electrodes (look out for **solid** reactants/products in half-equations).
- ⚙ Change in **pH** (look out for **H⁺** or **OH⁻** ions in half-equations).
- ⚙ **Bubbles** being formed (look out for **gases** being formed).
- ⚙ **Change in colour** (look out for **ions** being produced/consumed in solution).

Let's revisit the electrolysis of water example:

Question 12 Walkthrough.

List any observations made during the electrolysis of water.



➤ Observations:

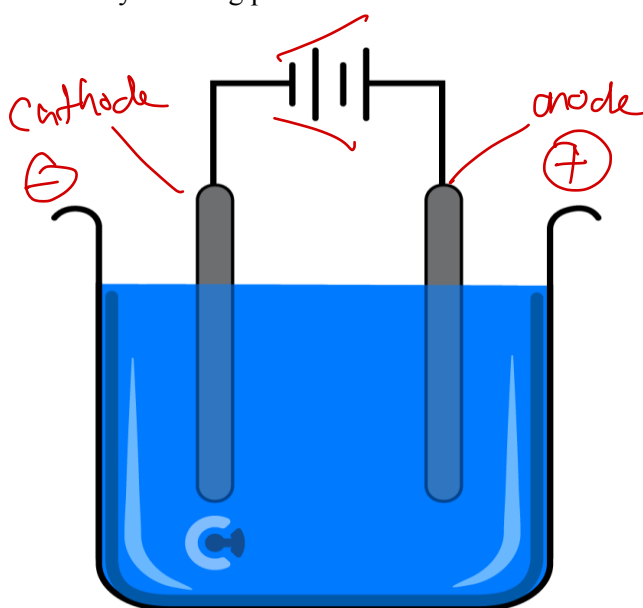
- ⚙ bubbles (H₂ formed) near cathode
- ⚙ bubbles (O₂ formed) near anode
- ⚙ water level decreases

NOTE: As they share an electrolyte and there is an increase in pH around one electrode, and a decrease in pH around the other electrode, there is **no pH change overall!**

ALSO NOTE: Water level decrease is a niche observation and should not be written first!

Question 13

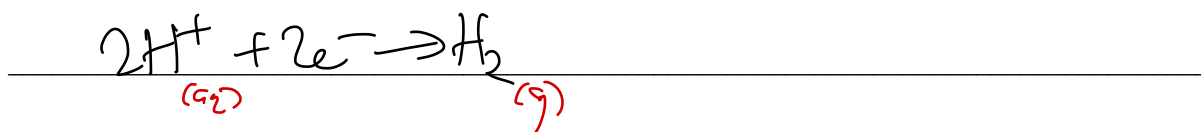
Hydrochloric acid (HCl(aq)) is electrolysed using platinum electrodes.



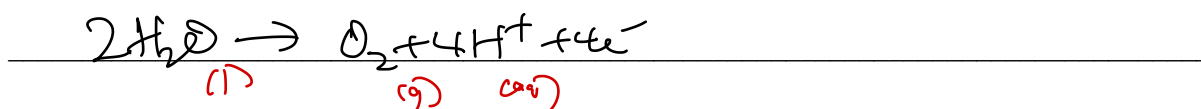
a. Label the cathode/anode in the diagram above, and label their polarities.

b. Write the balanced half-equation which occurs at the:

i. Cathode.



ii. Anode.

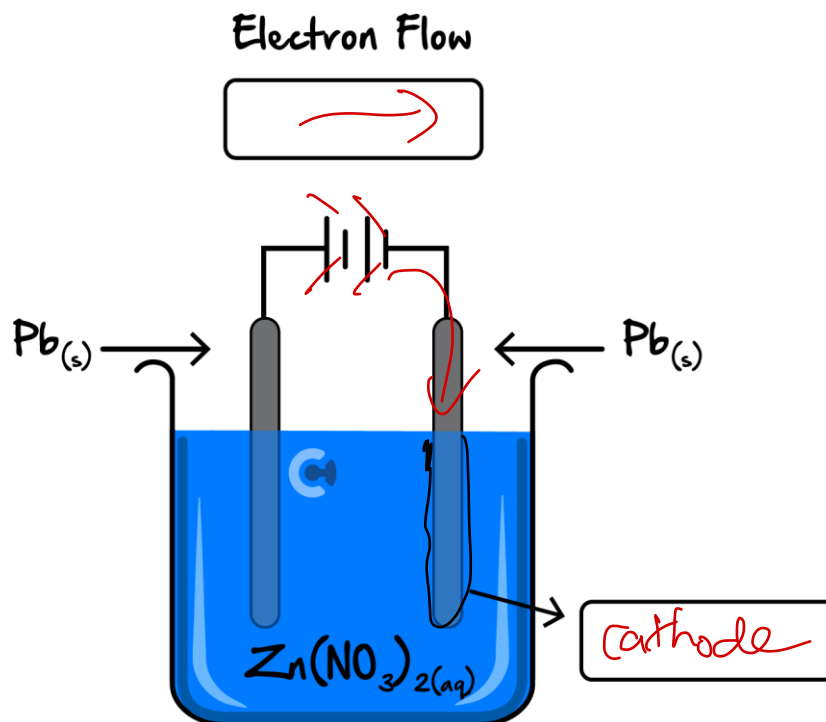


c. List any observations which can be made during this reaction.

- bubbles cathode ($H_{2(g)}$ formed)
- bubbles anode ($O_{2(g)}$ formed)

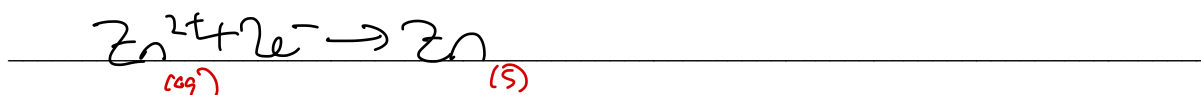
Question 14

The electrolysis of zinc nitrate ($\text{Zn}(\text{NO}_3)_2(\text{aq})$) solution is undertaken with solid lead ($\text{Pb}(\text{s})$) electrodes, according to the diagram below. Label the cathode/anode of the right electrode.

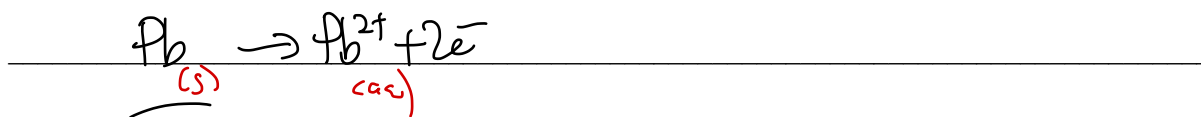


a. Write the balanced half-equation which occurs at the:

i. Cathode.



ii. Anode.



b. List any observations which can be made during this reaction.

- $\text{Zn}_{(\text{s})}$ coating forms on cathode
- ↓ size of Pb electrode

Space for Personal Notes



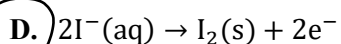
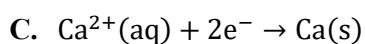
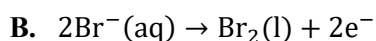
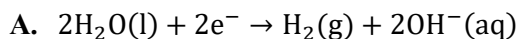
Question 15

Inspired from VCAA Chemistry Exam 2009

<https://www.vcaa.vic.edu.au/Documents/exams/chemistry/2009chem2-w.pdf#page=8>

An aqueous solution containing a mixture of 1.0 M KI and 1.0 M CaBr₂ was electrolysed using unreactive electrodes.

Which one of the following reactions is most likely to occur at the anode?



Question 16 Additional Question.

During the electrolysis of water, the pH of the solution will:

A. Decrease around the negative electrode and increase around the positive electrode.

B. Increase around the negative electrode and decrease around the positive electrode.

C. Decrease at both electrodes.

D. Increase at both electrodes.

Question 17 Additional Question.

A solution of green nickel nitrate and aluminium chloride is electrolysed by using graphite electrodes. Which of the following are **not** expected to be observed?

A. The size of the negative electrode increases. ✓

B. Bubbles are formed. ✓

C. The colour of the solution changes. ✓

D. The pH of the solution increases. ✗

Sub-Section: Electrolytic Cells Electrodes

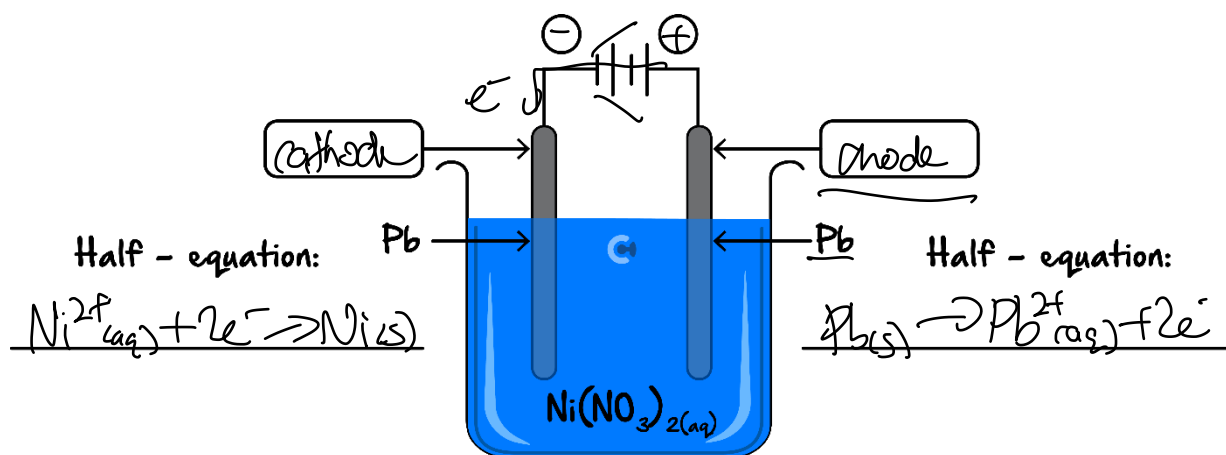


Context

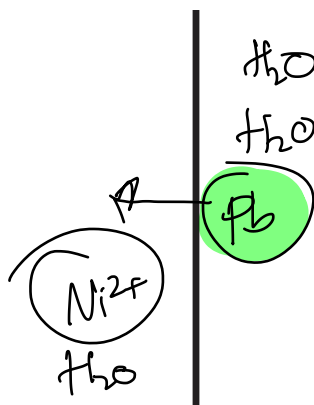
- There are times where the electrodes themselves are also comprised of a metal themselves.
- However, attention must be given to these sorts of situations.

Exploration: Electrolysis Setup Scenario #1

- First consider electrolysis of nickel (II) nitrate, using lead electrodes.
- Where is the cathode/anode? *(Label Below)*



Create the mini electrochemical series:



➤ What is the strongest oxidant and reductant? (Circle Above)

⚙ What type of reaction does the strongest reductant undergo? [reduction] / [oxidation]

⚙ Where does this strongest reductant react? [cathode] / [anode]

⚙ Is it present at the anode? [yes] / [no]

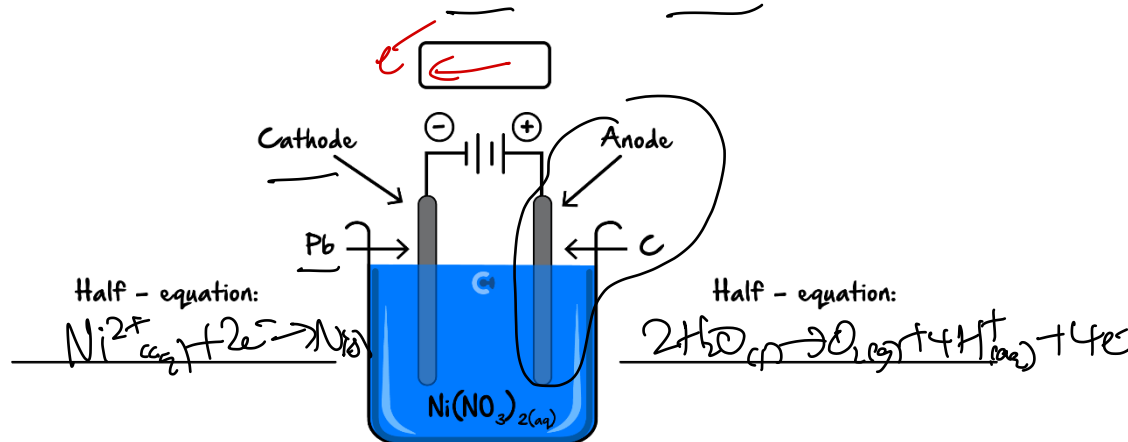
⚙ Can it react? [yes] / [no]

➤ What are the half-equations which take place? (Label in Diagram Above)

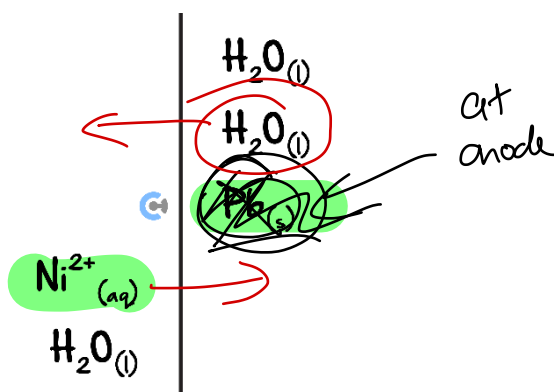
Now, let's consider a similar setup, but this time only the cathode has Lead solid!

Exploration: Electrolysis Setup Scenario #2

➤ Consider electrolysis of nickel nitrate, using lead only at the cathode. The anode is made of graphite.



⚙ Find the strongest oxidant and reductant on paper. (Label Below)



Strongest reductant undergoes oxidation at the anode.

Is Pb(s) present at the anode? [yes] / [no] Can this Pb(s) react at the anode? [yes] / [no]

➤ Reconsider the strongest oxidant and reductant which can actually react:

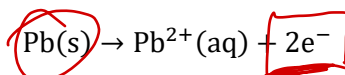
Strongest oxidant which can actually React	Strongest Reductant which can actually react
Ni^{2+}	H_2O

What is another way to think about it?

Analogy: Water Gun

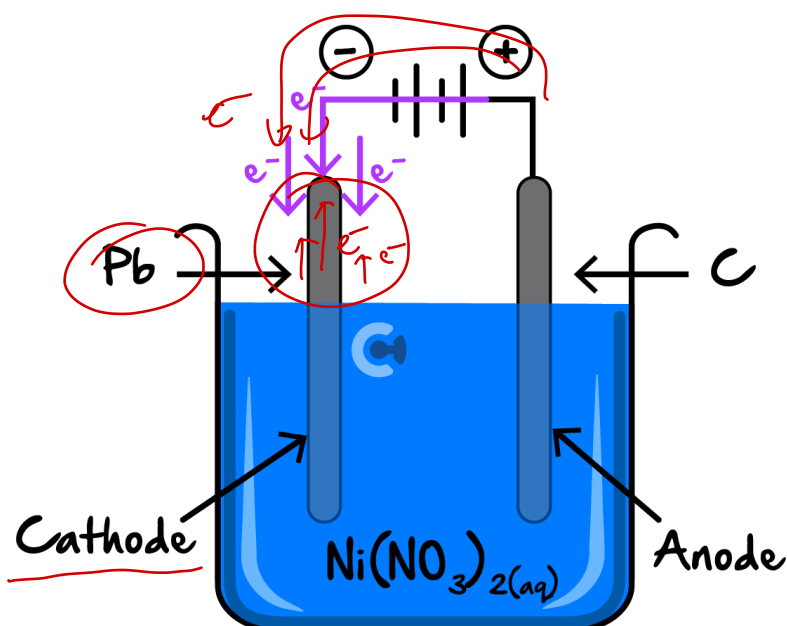
➤ If lead were to react...

➤ Half-Equation:



Electrons are [shot out] / [taken in]

➤ Consider the electrolytic cell. How would the electrons look like if it were to react? *(Label Below)*



- Think about the scenario like a waterfall:



Cathode Reactivity in Electrolysis



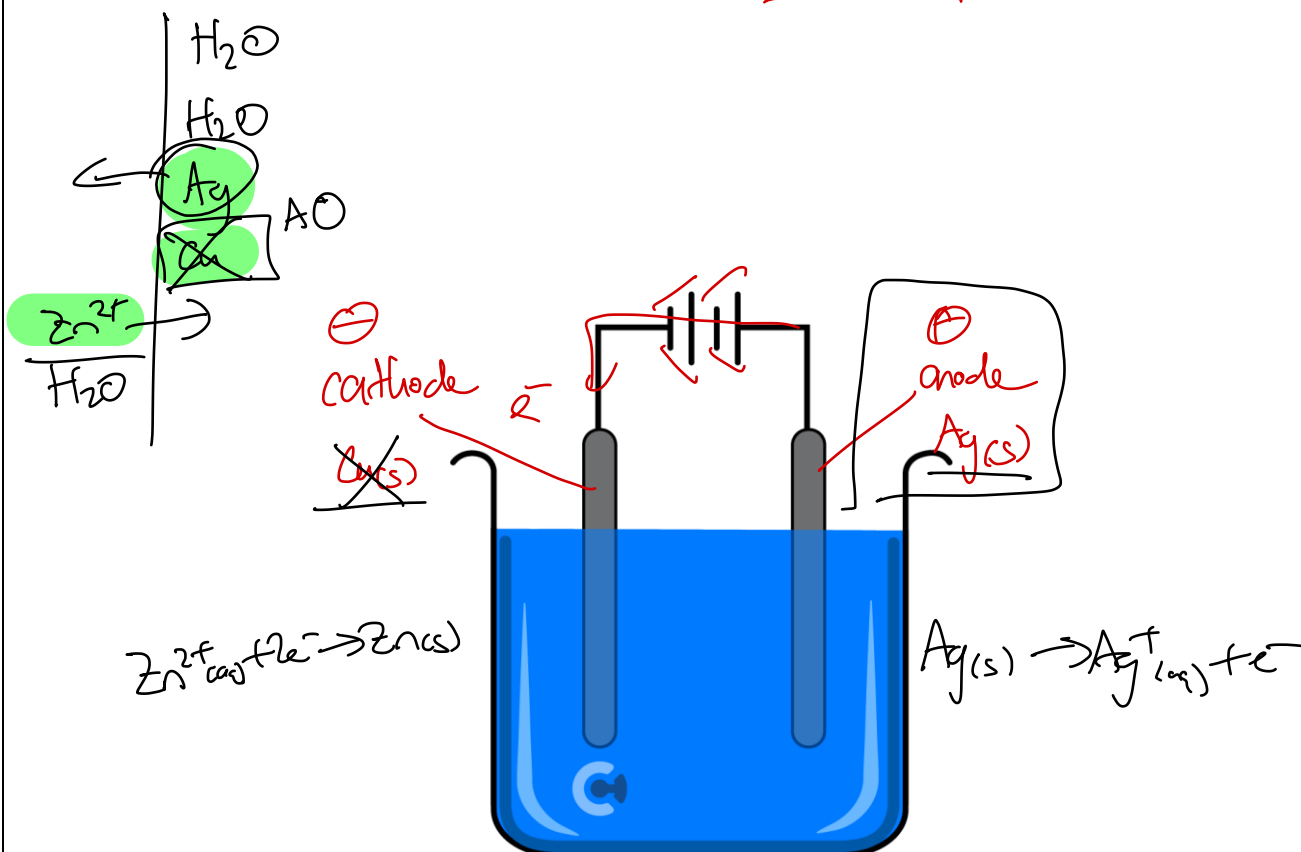
- Strongest Reductant must be present at the anode.
- Generally, metals at the cathode are considered unreactive and be ignored!

Space for Personal Notes

Let's have a look at one more scenario together!

Question 18 Walkthrough.

Draw a labelled cell for the electrolysis of $\text{Zn}(\text{NO}_3)_2(\text{aq})$ with a copper cathode and silver anode, writing out the half-equations.



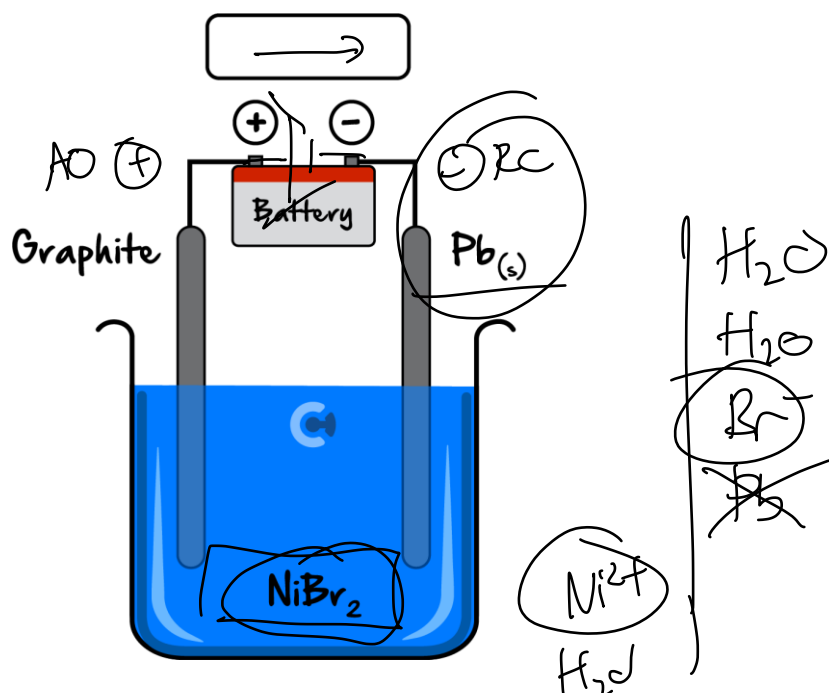
NOTE: Even though solid copper (Cu(s)) is the strongest reductant in this scenario, it is at the cathode which is the wrong electrode, and thus it cannot oxidise.

Space for Personal Notes

Your Turn!

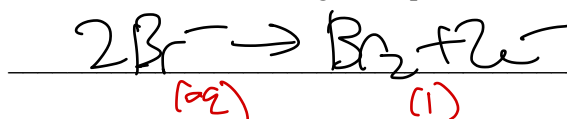
Question 19

A solution of nickel bromide, $\text{NiBr}_2(\text{aq})$ is electrolysed according to the set-up below. The graphite electrode is attached to the positive terminal of the power source, and the lead (Pb) electrode is attached to the negative terminal of the battery.

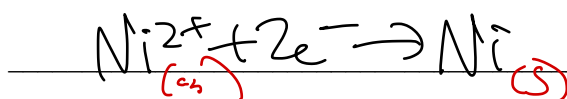


a. Write the equation for:

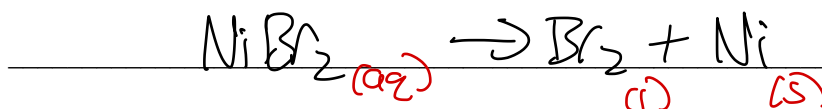
i. The half-reaction occurring at the positive electrode.



ii. The half-reaction occurring at the negative electrode.



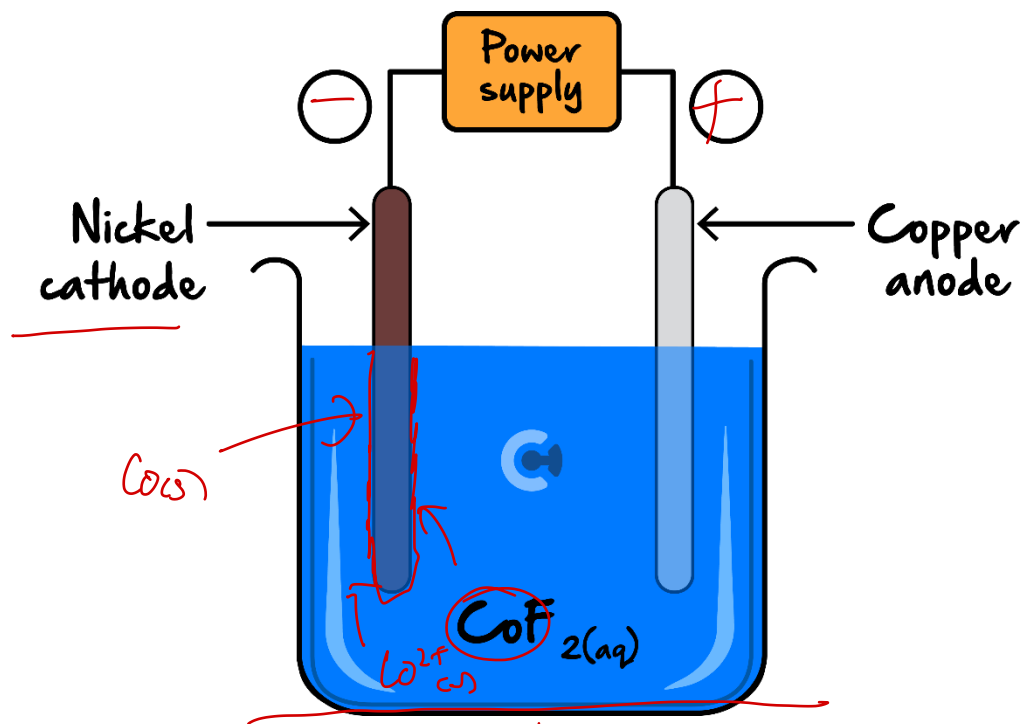
iii. The overall reaction.



b. Label the direction of the electron flow in the box above.

Question 20

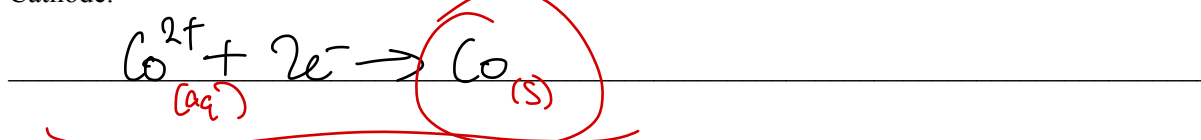
Daniel decides to construct an electrolytic cell for the electrolysis of cobalt fluoride $\text{CoF}_2(\text{aq})$ with a ~~nickel~~ ~~cathode~~ and copper anode, which is shown below.



a. Label the polarities of each electrode in the circles provided above.

b. Write the balanced half-equation which occurs at the:

i. Cathode.



ii. Anode.



c. The entire cell is placed on an electronic balance and its mass is monitored over time. The battery power source is not placed on the electronic balance (ignore the change in mass of the battery). Describe and justify the change in mass expected to be observed as the cell operates.

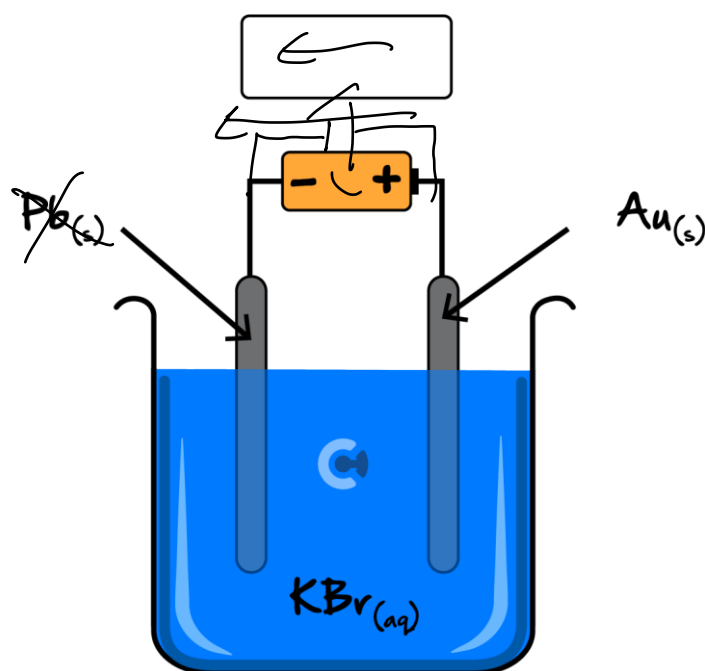
No change in mass. All reactants/products stay in cell, nothing entering/leaving.

NOTE: Different molar mass.
Nothing enters/leaves.



Question 21

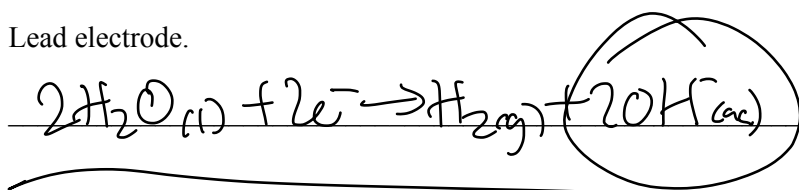
Ben decides to carry out an experiment to see what happens if he electrolyses a solution of potassium bromide (KBr), with the lead electrode, connected to the negative terminal of the battery and gold electrode connected to the positive terminal of the battery.



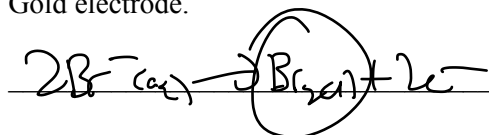
a. Label the direction of electron flow in the box provided above.

b. Write the half-equations which occurs at the:

i. Lead electrode.



ii. Gold electrode.



c. As the reaction proceeds, the electrolyte begins to turn brown. Provide an explanation for this observation.

$\text{Br}_2(l)$ is produced which is brown.

- d. When the experiment is started, a pH metre is dipped into the electrolytic cell and it reads a pH of 7. After 5.0 min, the pH metre is reinserted, and the pH reading is not 7. Justify whether it will be above or below 7.

pH increased at OH⁻ is produced making electrolyte more basic. Above 7.

Question 22 Additional Question.

Platinum electrodes are placed in a solution which contains zinc nitrate, $\text{Zn}(\text{NO}_3)_2$, and sodium chloride, NaCl , and is connected to a power source. Which one of the following statements about the reaction is correct?

- A. Zinc metal is produced at the anode and Chlorine gas is produced at the cathode.
- ☒ B. Zinc metal is produced at the cathode and Oxygen gas is produced at the anode.
- C. Sodium metal is produced at the anode and Chlorine gas is produced at the cathode.
- D. Sodium metal is produced at the cathode and Oxygen gas is produced at the anode.

Question 23 Additional Question.

An electrolytic cell which contains a solution of magnesium nitrate and sodium chloride is electrolysed. The positive terminal of the power source is attached to a gold electrode and the negative terminal is attached to a copper electrode. Which of the following is true?

- ☒ A. Both electrodes will have no change in mass/size.
- B. No bubbles will be observed.
- C. The overall pH increases.
- D. The overall pH decreases.

Space for Personal Notes

Sub-Section: Input of Voltage



Electrolytic cells require an input of energy in order to progress, but how much voltage (EMF) do we need to input?



Active Recall: How is the EMF of a cell calculated?

$$EMF = E^{\circ}(\text{oxidant}) - E^{\circ}(\text{reductant})$$

Exploration: EMF Required



- Consider the electrolysis of a 1.0 M solution of nickel chloride ($\text{NiCl}_2(\text{aq})$):
- What are the half-equations which occur at each electrode, along with its E° value?

Electrode	Half-Equation	E° Value
Cathode (-)	$\text{Ni}^{2+}_{(\text{aq})} + 2e^{-} \rightarrow \text{Ni}_{(\text{s})}$	-0.25V
Anode (+)	$2\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{O}_{2(\text{g})} + 4\text{H}^{+}_{(\text{aq})} + 4e^{-}$	1.23V

- **EMF:** ($EMF = E^{\circ}(\text{oxidant}) - E^{\circ}(\text{reductant})$) $\frac{-0.25 - 1.23\text{V}}{-1.48\text{V}}$
- **Meaning:** $\frac{-1.48\text{V}}{-1.48\text{V}}$
- **EMF Required for Cell to Operate:** $\frac{-1.48\text{V}}{>1.48\text{V}}$

Space for Personal Notes



Analogy: Myki



➤ If the balance in the myki is **positive**, can we touch on? ~~[yes]~~ [no]

⚙ If the **EMF is positive**, a **reaction** will occur.

➤ If the balance in the myki is **zero** or **negative**, can we touch on? [yes] / ~~[no]~~

⚙ If the **EMF is zero or negative**, **no reaction** will occur.

➤ Scenario: Myki Balance is -\$1.00, -1

➤ Top-Up Amount: \$1.01 -1.23

EMF For Electrolysis



$$EMF = E^0(\text{oxidant}) - E^0(\text{reductant})$$

➤ EMF Required is **greater than** ~~the difference in EMF.~~

Space for Personal Notes



Contour Checklist

- Learning Objective: [2.1.1] - Identify differences between galvanic & electrolysis for electrodes, energy conversions, electron flow

Study Design

"The 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

	Galvanic cells	Electrolytic cells
Spontaneous Reaction	[Yes] / [No]	[Yes] / [No]
Energy Conversion	chem \rightarrow elec	elec \rightarrow chem
Type of Reaction	[Exothermic] / [Endothermic]	[Exothermic] / [Endothermic]
Oxidant / Reductant Relative Strength		
Electron Flow	anode \rightarrow cathode	anode \rightarrow cathode
Anode	AO \ominus	AO \oplus
Cathode	RC \oplus	RC \ominus
Salt-Bridge / Electrolyte Ion Flow	Cations \rightarrow [cathode] / [anode]	Cations \rightarrow [cathode] / [anode]

- **Learning Objective: [2.1.2] - Write equations & calculate EMF required for electrolytic reactions**

Key Takeaways

- When predicting electrolytic reactions, do not forget to include H₂O.
- Metals at the cathode are unreactive.
- Voltage Required is more than difference.



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

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