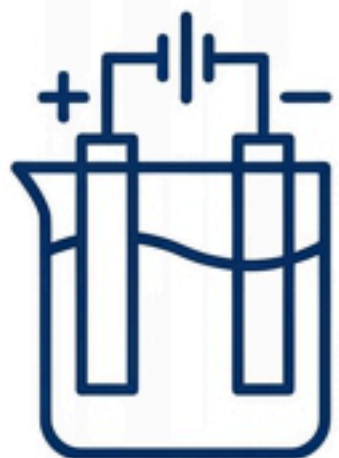




CHAPTER 2 • ELECTROCHEMISTRY

2.5.1 Products of Electrolysis

Decoding the rules of ion competition, electrode nature, and overpotential.

Two Variables Dictate the Output



The Electrolyte State

The products depend on whether the electrolyte is molten (fused) or dissolved in water (aqueous).

Aqueous solutions introduce competing H^+ and OH^- ions from water.



The Electrode Nature

The products shift dramatically based on whether the physical electrodes react with the solution or simply conduct electricity.

We classify electrodes into two strict categories: Inert and Reactive.

The Role of the Electrode: Inert vs. Reactive



Inert Electrodes

Do not participate in the chemical reaction. They act purely as a source or sink for electrons.

Platinum (Pt), Gold (Au)



Reactive Electrodes

Participate directly in the electrode reactions. The electrode itself may dissolve or accumulate material.

Copper (Cu), Silver (Ag)

Rule of Thumb: If the electrode is inert, we only evaluate the ions in the electrolyte.



You've Learned the Theory. Let's Test Them Now.

$$E=mc^2$$



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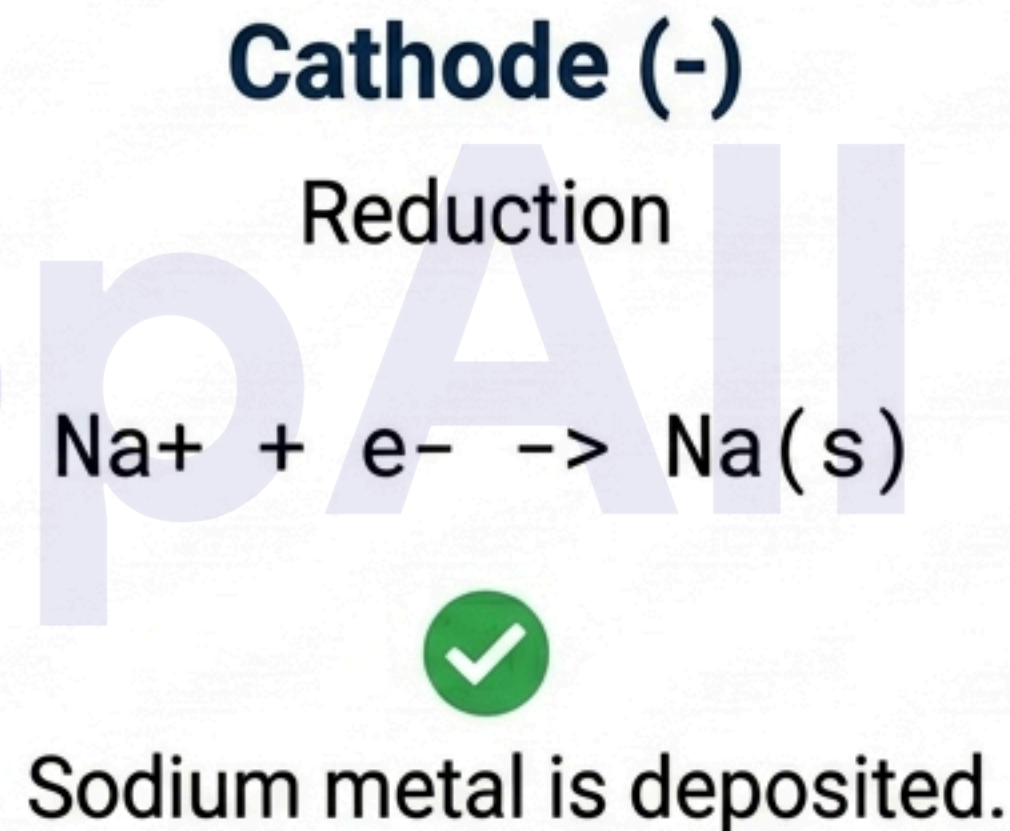
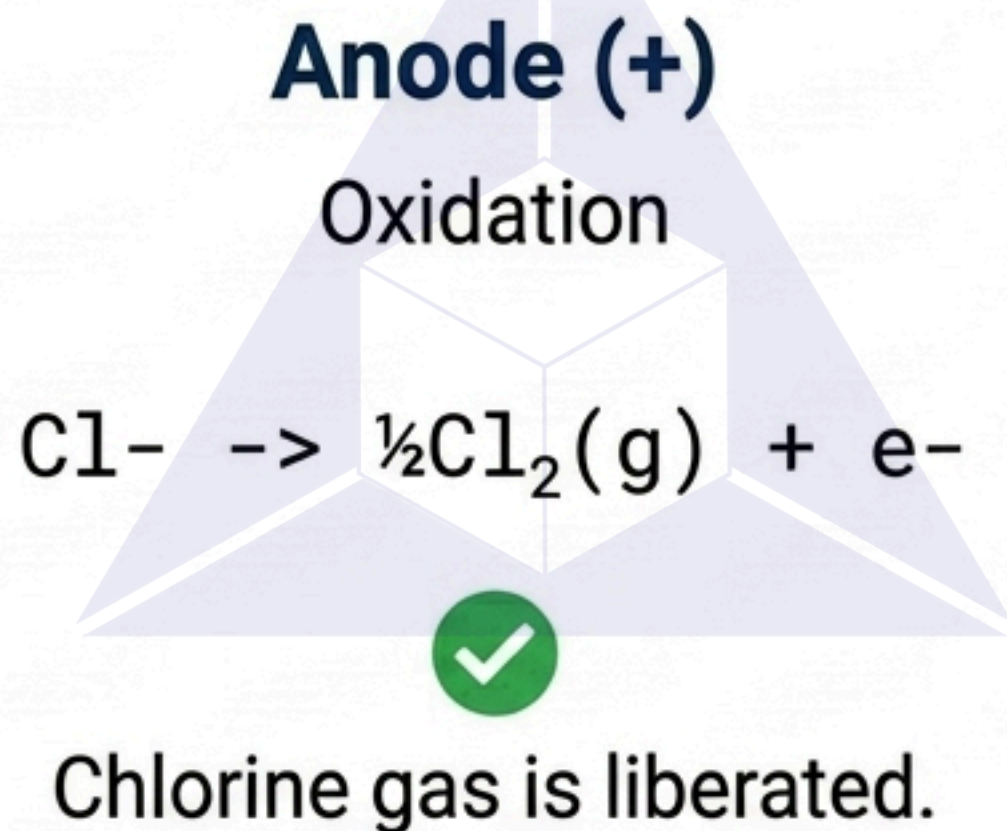
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Baseline Scenario: Molten NaCl (No Competition)

Fused/Molten state means strictly two ions exist: $[\text{Na}^+]$ and $[\text{Cl}^-]$. No water is present.



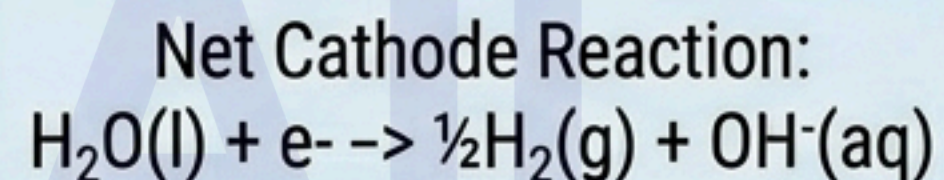
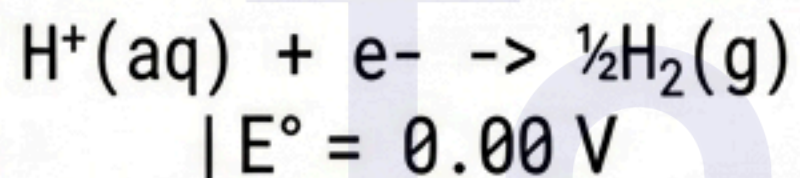
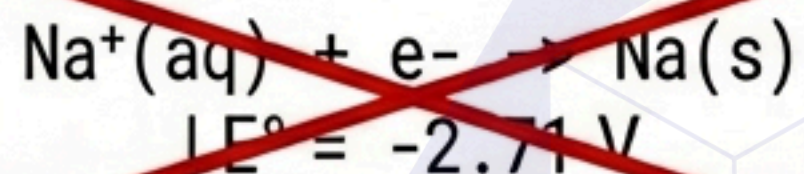
Diagnostic Result: With no other species present, the outcome is highly predictable and purely based on the source ions.

Aqueous NaCl: The Battle of Competing Species

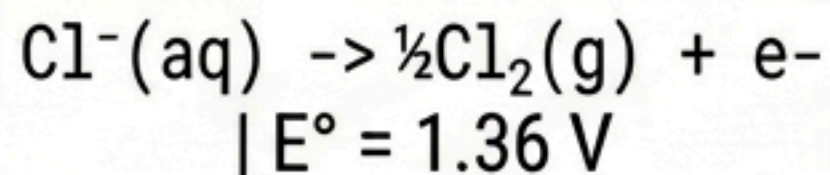
Water (H₂O) introduces H⁺ and OH⁻ into the arena, creating a competition decided by E° values.

Tournament Brackets

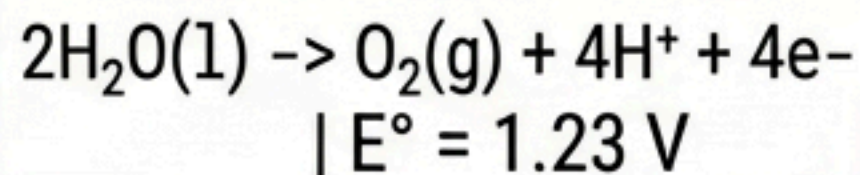
Cathode Bracket (Reduction: Higher E° Wins)



Anode Bracket (Oxidation: Lower E° Wins)



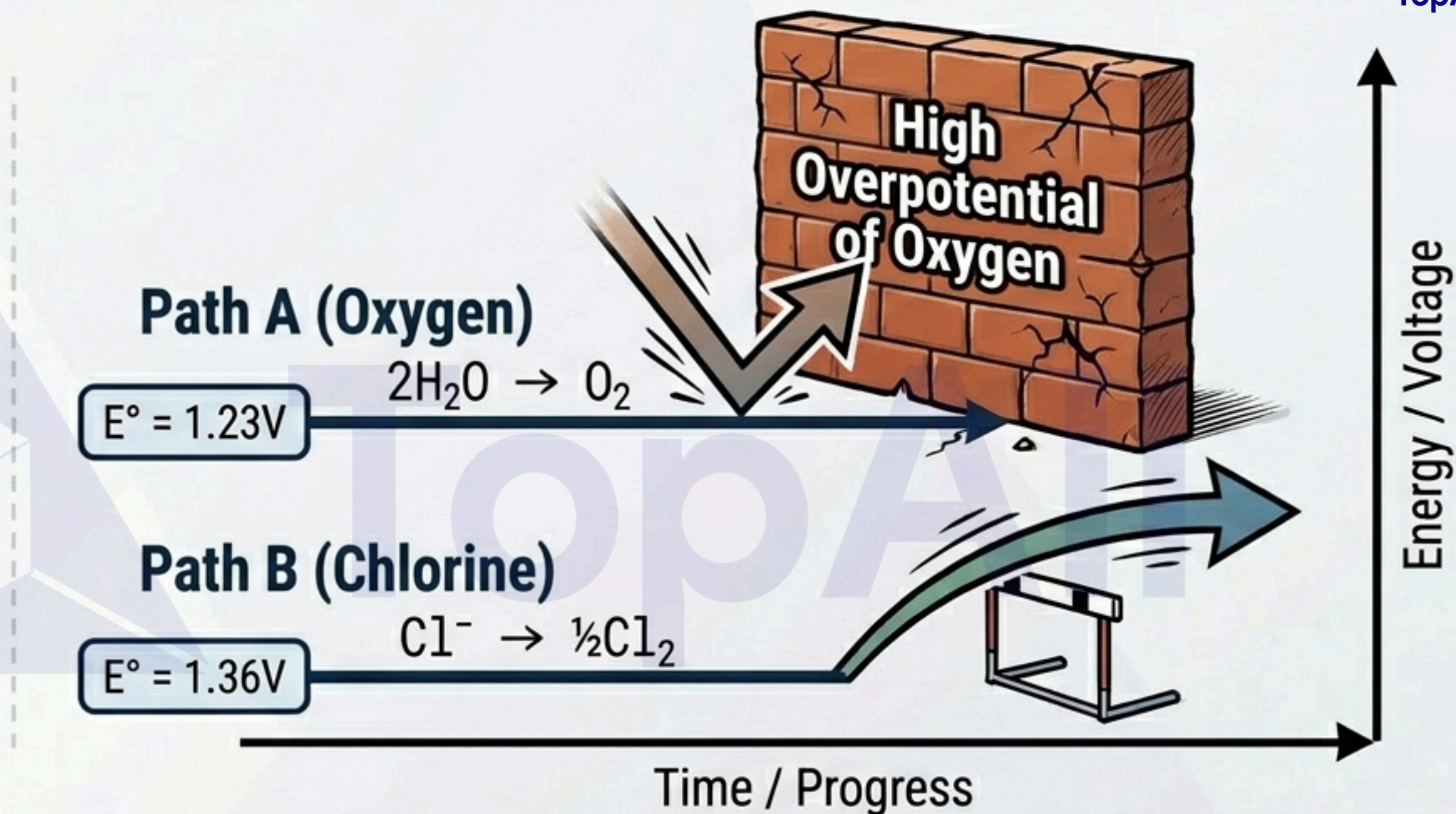
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By thermodynamic rules, H₂O has the lower E° and should win. But reality is different...

The Exception to the Rule: Overpotential

Some feasible electrochemical processes are kinetically so slow that they require extra voltage to push them forward. This barrier is called **overpotential**.



Diagnostic Result: Because of the overpotential required to produce oxygen from water, the oxidation of Cl^- becomes the kinetically preferred path.

Result at Anode: $\frac{1}{2}\text{Cl}_2(\text{g})$ is produced.

Synthesis: How Medium Dictates the Product

Electrolyte System	Cathode (-) Product	Anode (+) Product
Molten NaCl (Inert Pt)	Na (s)	Cl ₂ (g)
Aqueous NaCl (Inert Pt)	H ₂ (g)	Cl ₂ (g)

Net Aqueous Equation: $\text{NaCl(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq}) + \frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g})$

The Ultimate Takeaway

The presence of an aqueous medium shifts the cathode product from a metal to hydrogen gas due to E° competition, while kinetic overpotential dictates the anode product.



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