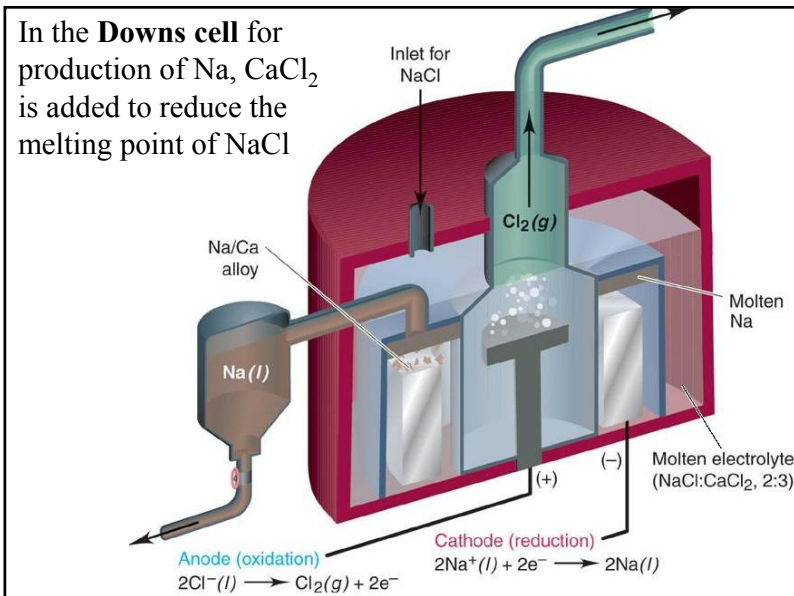
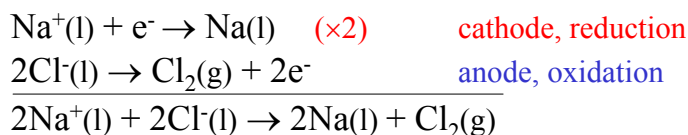


Predicting the Products of Electrolysis

- The **cations** (+) are attracted to the **cathode** (-) and the **anions** (-) are attracted to the **anode** (+)
- **Electrolysis of molten salts** – used for industrial isolation of the most active elements (Na, Li, Mg, Al, ...; F₂, Cl₂, Br₂, ...)
- The **cation** is reduced at the **cathode**
- The **anion** is oxidized at the **anode**

Example: Isolation of Na and Cl₂ by electrolysis of molten NaCl



Electrolysis of mixed molten salts

- The **cation** with higher *E*^o value (the **stronger oxidizing agent**) is reduced at the **cathode**
- The **anion** with lower *E*^o value (the **stronger reducing agent**) is oxidized at the **anode**

Note: *E*^o values in appendix D are for aqueous ions and can be used only as approximate guidance. Instead, *EN* values can be used to estimate the stronger oxidizing and reducing agents.

Example: Predict the products of the electrolysis of a molten mixture of NaCl and AlF₃

→ Possible **cathode** half-reactions (**reduction**)

- 1) Reduction of Na⁺ and
- 2) Reduction of Al³⁺

→ Al³⁺ is the stronger oxidizing agent because Al is more *EN* than Na, so Al³⁺ gains electrons easier

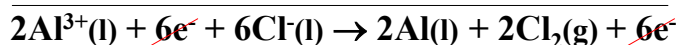
⇒ **Cathode** half-reaction: Al³⁺(l) + 3e⁻ → Al(l)

→ Possible **anode** half-reactions (**oxidation**)

- 1) Oxidation of F⁻ and
- 2) Oxidation of Cl⁻

→ Cl⁻ is the stronger reducing agent because Cl is less *EN* than F, so Cl⁻ loses electrons easier

⇒ **Anode** half-reaction: 2Cl⁻(l) → Cl₂(g) + 2e⁻

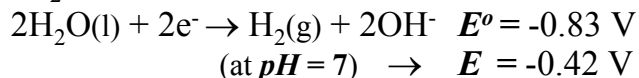


⇒ The products are Al(l) and Cl₂(g)

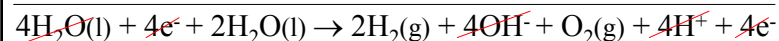
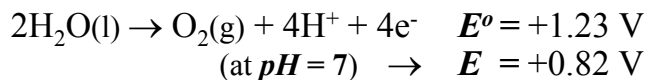
• Electrolysis of water

– Pure water is hard to electrolyze (low conductivity), so a small amount of a non-reactive salt (NaNO_3) is added (can be neglected)

→ H_2O is reduced at the **cathode**:



→ H_2O is oxidized at the **anode**:



→ Overall: $2\text{H}_2\text{O(l)} \rightarrow 2\text{H}_2\text{(g)} + \text{O}_2\text{(g)}$

$$E_{\text{cell}} = E_{\text{cath}} - E_{\text{anod}} = -0.42 - (+0.82) = -1.24 \text{ V}$$

→ $E_{\text{cell}} < 0 \Rightarrow$ non-spontaneous reaction

$\Rightarrow$ To drive the reaction, the external voltage must be greater than 1.24 V

• **Overvoltage** – the extra voltage (in the case of water over 1.24) needed to drive the reaction

– For H_2O on most inert electrodes, the overvoltage is **0.4 to 0.6 V per electrode**

→ Cathode, reduction:

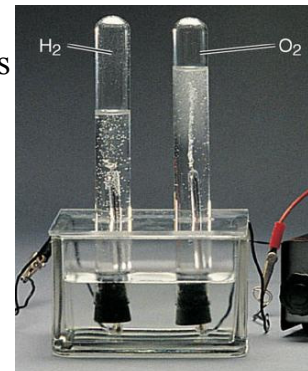
$$E = -0.42 - 0.6 \approx -1.0 \text{ V}$$

→ Anode, oxidation:

$$E = +0.82 + 0.6 \approx +1.4 \text{ V}$$

→ Total:

$$E_{\text{cell}} = -1.0 - (+1.4) \approx -2.4 \text{ V}$$



• Electrolysis of aqueous solutions

→ Possible **cathode** half-reactions (**reduction**)

1. Reduction of H_2O
2. Reduction of **cations** in the solution

→ Possible **anode** half-reactions (**oxidation**)

1. Oxidation of H_2O
2. Oxidation of **active metal electrodes**
3. Oxidation of **anions** in the solution

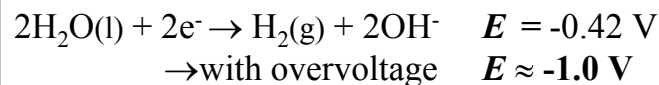
→ The half-reaction with the **higher E° value** (having the stronger oxidizing agent) **occurs on the cathode**

→ The half-reaction with the **lower E° value** (having the stronger reducing agent) **occurs on the anode**

Example: Predict the products of the electrolysis of a mixture of 1M NaCl(aq) and 1M $\text{KNO}_3\text{(aq)}$ with inert electrodes at $\text{pH} = 7$.

→ Possible **cathode** half-reactions (**reduction**)

1. Reduction of H_2O



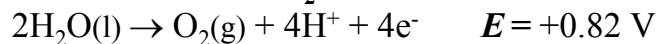
2. Reduction of **cations** in the solution



→ Half-reaction (1) has the highest (most positive) E value $\Rightarrow$ **H_2O is reduced** to H_2 on the **cathode**

→ Possible **anode** half-reactions (**oxidation**)

1. Oxidation of **H₂O**



→ with overvoltage $E \approx +1.4 \text{ V}$

2. Oxidation of **active metal electrodes** – none

3. Oxidation of **anions** in the solution

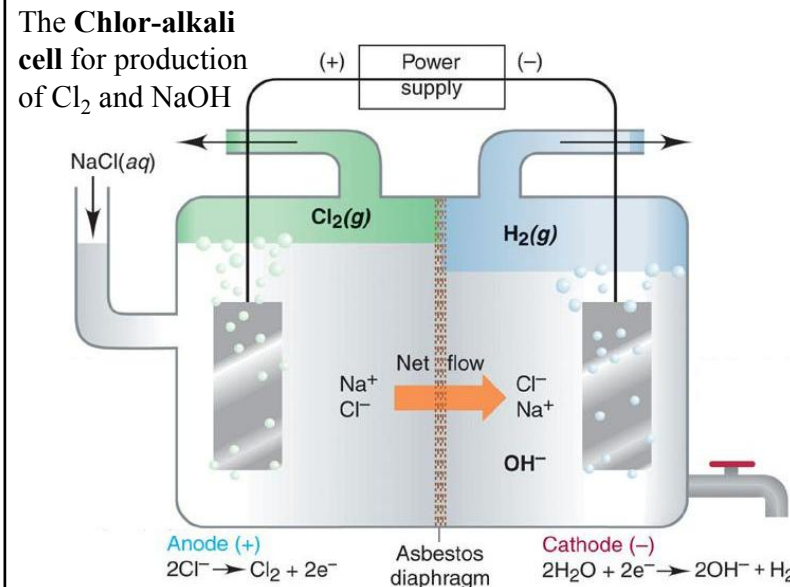


Note: NO₃³⁻ can't be further oxidized (not a product in any half-reaction in appendix D)

→ Half-reaction (3) has the lowest E° value ⇒ **Cl⁻ is oxidized** to Cl₂ on the **anode**

→ Overall: **2H₂O(l) + 2Cl⁻ → H₂(g) + 2OH⁻ + Cl₂(g)**

Note: Without the overvoltage, H₂O would be oxidized to O₂ at the anode



➤ Electrolysis of aqueous solutions is often used for production or purification of less active elements

➤ Cations of **less active metals** (Cu, Ag, Au, Pt, ...) **are reduced** on the cathode

➤ Anions of **less active nonmetals** (I₂, Br₂, ...) **are oxidized** on the anode (including Cl₂ due to the overvoltage of water)

➤ Cations of **more active metals** (Na, K, Mg, Ca, ...) **are not reduced** (H₂O is reduced to H₂ instead) → can't be produced by electrolysis of aqueous soln.

➤ Anions of **more active nonmetals** (F⁻) and **oxoanions of elements in their highest oxidation state** (NO₃⁻, CO₃²⁻, SO₄²⁻, ...) **are not oxidized**

The Stoichiometry of Electrolysis

- **Faraday's law** – the amount of substance produced on each electrode is directly proportional to the amount of charge transferred through the cell

I → el. current

t → time of electrolysis

Q → charge transferred

n → # mol e⁻ transferred

$$I = Q/t \rightarrow Q = I \times t$$

$$Q = nF \rightarrow n = Q/F$$

$$\Rightarrow n = \frac{I \times t}{F}$$

→ n is related to the amount of substance through the stoichiometry of the half-reaction

→ Allows the determination of the amount of substance produced by measuring I and t

Example: During electrorefining of Cu, how much time is needed to produce **250 g** Cu on the cathode if the current is kept at **11 A**?

$$I = 11 \text{ A} = 11 \text{ C/s} \quad t \rightarrow ?$$

Half-reaction: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu(s)}$

$$n = 250 \text{ g} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \times \frac{2 \text{ mol e}^-}{1 \text{ mol Cu}} = 7.9 \text{ mol}$$

$$n = \frac{I \times t}{F} \Rightarrow t = \frac{n \times F}{I}$$

$$t = \frac{7.9 \text{ mol} \times 96485 \text{ C/mol}}{11 \text{ C/s}} = 6.9 \times 10^4 \text{ s} = 19 \text{ hr}$$

Electrorefining of Cu

