Predicting the Products of Electrolysis
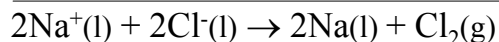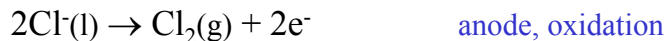
  – The cations (+) are attracted to the cathode (-) and the anions (-) are attracted to the anode (+)

- **Electrolysis of molten salts –** used for industrial isolation of the most active elements (Na, Li, Mg, Al, …; F_2, Cl_2, Br_2, …)
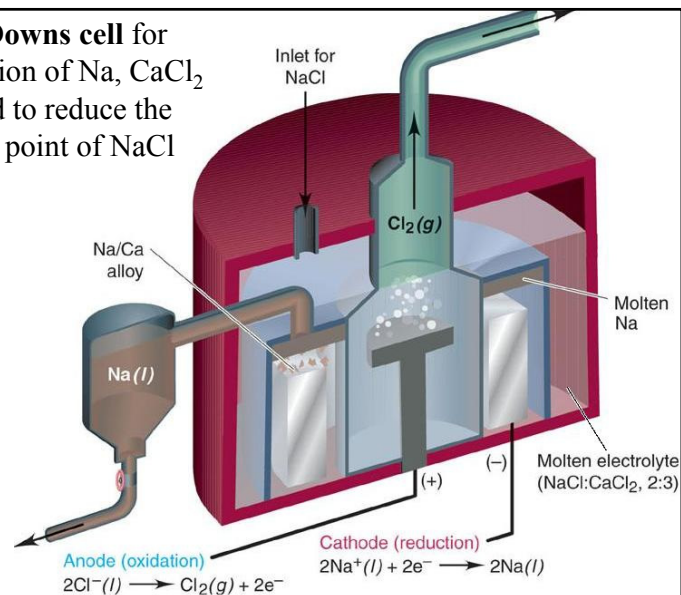
  – The cation is reduced at the cathode
  – The anion is oxidized at the anode

Example: Isolation of Na and Cl_2 by electrolysis of molten NaCl

$$Na^+(l) + e^- \rightarrow Na(l) \quad (\times 2) \qquad \text{cathode, reduction}$$
$$2Cl^-(l) \rightarrow Cl_2(g) + 2e^- \qquad \text{anode, oxidation}$$
$$\overline{2Na^+(l) + 2Cl^-(l) \rightarrow 2Na(l) + Cl_2(g)}$$

In the **Downs cell** for production of Na, $CaCl_2$ is added to reduce the melting point of NaCl

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- **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 AlF_3
→ Possible cathode half-reactions (reduction)
  1) Reduction of Na^+ and **2)** Reduction of Al^{3+}

→Al^{3+} is the stronger oxidizing agent because Al is more EN than Na, so Al^{3+} gains electrons easier
$\Rightarrow$ Cathode half-reaction: $Al^{3+}(l) + 3e^- \rightarrow Al(l)$

→ 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^- looses electrons easier
  $\Rightarrow$ Anode half-reaction: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

$Al^{3+}(l) + 3e^- \rightarrow Al(l) \qquad (\times 2) \quad$ cathode, reduction
$2Cl^-(l) \rightarrow Cl_2(g) + 2e^- \qquad (\times 3) \quad$ anode, oxidation
$\overline{2Al^{3+}(l) + 6e^- + 6Cl^-(l) \rightarrow 2Al(l) + 3Cl_2(g) + 6e^-}$
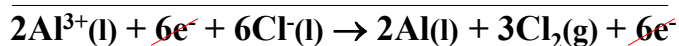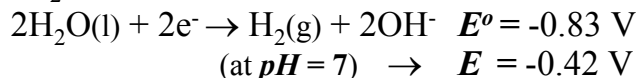
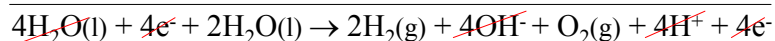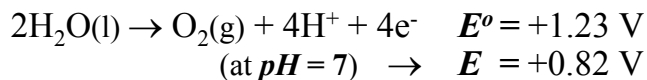$\Rightarrow$ The products are **Al(l)** and **$Cl_2(g)$**

- **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)
- $\rightarrow H_2O$ is reduced at the cathode:

  $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-$ $E^o = -0.83$ V

  (at $pH = 7$) $\rightarrow$ $E = -0.42$ V
- $\rightarrow H_2O$ is oxidized at the anode:

  $2H_2O(l) \rightarrow O_2(g) + 4H^+ + 4e^-$ $E^o = +1.23$ V

  (at $pH = 7$) $\rightarrow$ $E = +0.82$ V

  $\overline{4H_2O(l) + 4e^- + 2H_2O(l) \rightarrow 2H_2(g) + 4OH^- + O_2(g) + 4H^+ + 4e^-}$
- $\rightarrow$ Overall: $\mathbf{2H_2O(l) \rightarrow 2H_2(g) + O_2(g)}$

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

- $\rightarrow E_{cell} < 0 \Rightarrow$ 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**
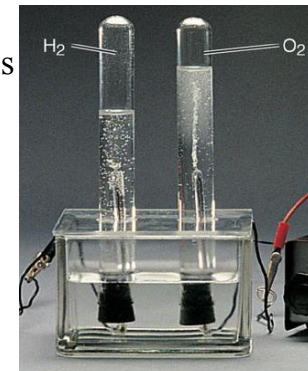- $\rightarrow$ Cathode, reduction:

  $E = -0.42 - 0.6 \approx \mathbf{-1.0\ V}$
- $\rightarrow$ Anode, oxidation:

  $E = +0.82 + 0.6 \approx \mathbf{+1.4\ V}$
- $\rightarrow$ Total:

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

- **Electrolysis of aqueous solutions**
- $\rightarrow$ Possible cathode half-reactions (reduction)
  1. Reduction of $\mathbf{H_2O}$
  2. Reduction of **cations** in the solution
- $\rightarrow$ Possible anode half-reactions (oxidation)
  1. Oxidation of $\mathbf{H_2O}$
  2. Oxidation of **active metal electrodes**
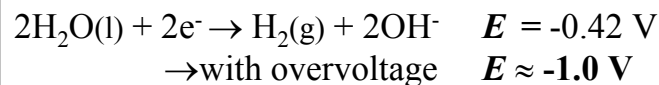 3. Oxidation of **anions** in the solution
- $\rightarrow$ The half-reaction with the **higher E^o value** (having the stronger oxidizing agent) **occurs on** the **cathode**
- $\rightarrow$ The half-reaction with the **lower E^o value** (having the stronger reducing agent) **occurs on** the **anode**

Example: Predict the products of the electrolysis of a mixture of 1M NaCl(aq) and 1M KNO_3(aq) with inert electrodes at $pH = 7$.

- $\rightarrow$ Possible cathode half-reactions (reduction)
  1. Reduction of $\mathbf{H_2O}$

  $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-$ $E = -0.42$ V

  $\rightarrow$ with overvoltage $E \approx \mathbf{-1.0\ V}$

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

  $Na^+ + e^- \rightarrow Na(s)$ $E^o = \mathbf{-2.71\ V}$

  $K^+ + e^- \rightarrow K(s)$ $E^o = \mathbf{-2.93\ V}$

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

→ Possible anode half-reactions (oxidation)

1. Oxidation of H_2O

$2H_2O(l) \rightarrow O_2(g) + 4H^+ + 4e^-$ $E = +0.82$ V

    → with overvoltage $E \approx +1.4$ V
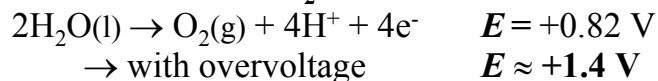
2. Oxidation of **active metal electrodes – none**

3. Oxidation of **anions** in the solution
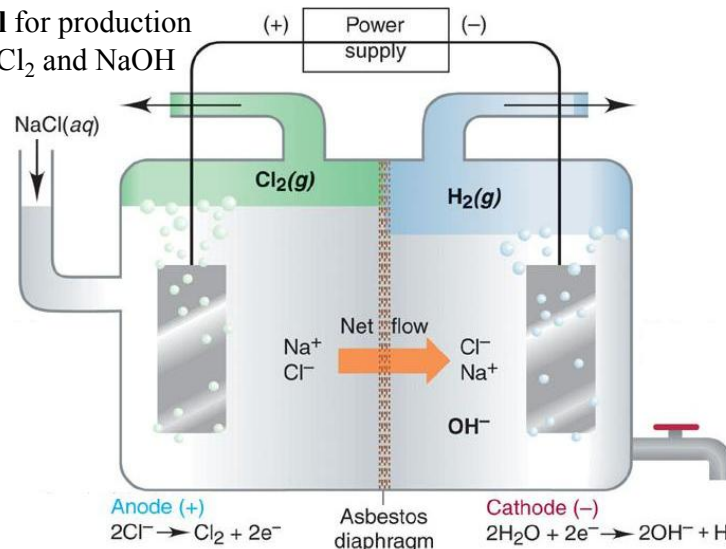
$2Cl^- \rightarrow Cl_2(g) + 2e^-$ $E^o = +1.36$ V

Note: NO^{3-} can't be further oxidized (not a product in any half-reaction in appendix D)

→ Half-reaction **(3)** has the lowest E^o value $\Rightarrow$ **Cl^- is oxidized** to Cl_2 on the **anode**

→ Overall: $\mathbf{2H_2O(l) + 2Cl^- \rightarrow H_2(g) + 2OH^- + Cl_2(g)}$

Note: Without the overvoltage, H_2O would be oxidized to O_2 at the anode

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The **Chlor-alkali cell** for production of Cl_2 and NaOH

➤ 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** (I_2, Br_2, …) **are oxidized** on the anode (including Cl_2 due to the overvoltage of water)

    ➤ Cations of **more active metals** (Na, K, Mg, Ca, …) **are not reduced** (H_2O is reduced to H_2 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** (NO_3^-, CO_3^{2-}, SO_4^{2-}, …) **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

    $I \rightarrow$ el. current $t \rightarrow$ time of electrolysis

    $Q \rightarrow$ charge transferred $n \rightarrow$ # mol e^- transferred

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

    $Q = nF \rightarrow \quad n = Q/F$ $\Rightarrow \quad \boxed{n = \dfrac{I \times t}{F}}$

→ 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**?

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

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

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

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

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

Elctrorefining of Cu

Cathode (−): $Cu^{2+} + 2e^- \rightarrow Cu$

Anode (+): $Cu \rightarrow Cu^{2+} + 2e^-$

Pure copper | Anode mud | Acidified $CuSO_4(aq)$ | Impure copper