Electrolysis of Compounds and Solutions

- Electrolysis of molten ionic compounds
- Electrolysis of aqueous solutions
- Summary activities
What is electrolysis?

An ionic compound can be split into its elements by passing an electric current through it. This is electrolysis. The substance the electric current passes through is called the electrolyte.

An ionic compound contains charged particles called ions. An ion is an atom that has gained or lost electrons and so carries a positive or negative charge. This charge is shown after its formula.

Ions with a positive charge have lost electrons, and ions with a negative charge have gained electrons.
Binary ionic compounds are composed of two different types of elements. When molten or dissolved in solution, these compounds can be split into their elements using electrolysis:

Negative ions move to the positive electrode (anode) and lose electrons. This is oxidation.

Positive ions move to the negative electrode (cathode) and gain electrons. This is reduction.

Non-metal elements form at the positive electrode.

Metal elements form at the negative electrode.
Electrolysis of molten lead bromide

A molten ionic compound can be split into its elements by passing an electric current through it. This is called electrolysis.

Press “play” to find out what happens in the electrolysis of molten lead bromide.
What redox processes occur at the electrodes during the electrolysis of molten lead bromide ($\text{PbBr}_2$)?

At the negative electrode:
\[ \text{Pb}^{2+}(\text{aq}) + 2e^- \rightarrow \text{Pb}(\text{l}) \] (reduction)

At the positive electrode:
\[ 2\text{Br}^-(\text{aq}) \rightarrow \text{Br}_2(\text{g}) + 2e^- \] (oxidation)

What is the overall equation for the electrolysis of molten lead bromide?

\[ \text{PbBr}_2(\text{l}) \rightarrow \text{Pb}(\text{l}) + \text{Br}_2(\text{g}) \]
Extracting aluminium from its ore

Electrolysis can be used to **extract** reactive metals from their molten form.

For example, aluminium is extracted from its ore, **bauxite**, by first purifying the bauxite to aluminium oxide \((\text{Al}_2\text{O}_3)\).

The aluminium oxide is heated to very high temperatures to form a molten compound. This allows an electric current to be passed through it.

The aluminium metal is produced at the negative electrode. It sinks to the bottom of the tank where it can be removed. Oxygen gas forms at the positive electrode.
Electrolysis of $\text{Al}_2\text{O}_3$ – redox equations

Positive aluminium ions move to the negative electrode where they gain electrons:

$$4\text{Al}^{3+}(\text{aq}) + 12e^- \rightarrow 4\text{Al}(s) \text{ (reduction)}$$

Oxygen ions move to the positive electrode where they lose electrons and form oxygen gas:

$$6\text{O}^2-(\text{aq}) \rightarrow 3\text{O}_2(g) + 12e^- \text{ (oxidation)}$$

The oxygen molecules react with the carbon electrode, producing carbon dioxide. This means the graphite electrodes must be continually replaced.

What is the overall equation for the electrolysis of molten lead bromide?

$$\text{aluminium oxide} \rightarrow \text{aluminium} + \text{oxygen}$$

$$2\text{Al}_2\text{O}_3(l) \rightarrow 4\text{Al}(s) + 3\text{O}_2(g)$$
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Electrolysis of aqueous solutions

During electrolysis of aqueous solutions, the ions which are **discharged** (gain or lose electrons) depends on the relative **reactivity** of the elements involved.

<table>
<thead>
<tr>
<th>reactivity series</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium</td>
</tr>
<tr>
<td>Sodium</td>
</tr>
<tr>
<td>Calcium</td>
</tr>
<tr>
<td>Magnesium</td>
</tr>
<tr>
<td>Aluminium</td>
</tr>
<tr>
<td>Zinc</td>
</tr>
<tr>
<td>Iron</td>
</tr>
<tr>
<td>Lead</td>
</tr>
<tr>
<td><strong>Hydrogen</strong></td>
</tr>
<tr>
<td>Copper</td>
</tr>
<tr>
<td>Silver</td>
</tr>
<tr>
<td>Gold</td>
</tr>
<tr>
<td>Platinum</td>
</tr>
</tbody>
</table>

If the metal ion is more reactive than hydrogen, then hydrogen is produced at the negative electrode.

If the metal ion is less reactive than hydrogen, the metal element is formed at the negative electrode.

The ions are competing at the electrodes.

Oxygen is produced at the positive electrode.
Electrolysis of water

The presence of water in an aqueous salt solution affects the products of electrolysis.

This is because in aqueous solutions the water molecules break down:

$$ \text{H}_2\text{O (l)} \rightarrow \text{H}^+ (\text{aq}) + \text{OH}^- (\text{aq}) $$

During electrolysis, the hydrogen ($\text{H}^+$) and hydroxide ($\text{OH}^-$) ions are separated.

The hydrogen ion competes with the positive metal ion at the negative electrode.

The $\text{OH}^-$ ions are discharged at the positive electrode to produce oxygen.
Redox equations - water

What happens at the electrodes during the electrolysis of water?

At the negative electrode:

\[ 2H^+ + 2e^- \rightarrow H_2 \text{ (reduction)} \]

At the positive electrode:

\[ 4OH^- \rightarrow 2H_2O + O_2 + 4e^- \text{ (oxidation)} \]

What is the overall equation for the electrolysis of water?

\[ 2H_2O (l) \rightarrow 2H_2 (g) + O_2 (g) \]
Electrolysis of aqueous copper sulfate

What are the products during the electrolysis of aqueous copper sulfate?

- Solid copper is produced at the negative electrode.
  
  Copper is **less reactive** than hydrogen. This means the copper ions are preferentially discharged to produce copper:

  \[ \text{Cu}^{2+} (\text{aq}) + 2e^- \rightarrow \text{Cu}(\text{s}) \] (reduction)

- Oxygen (O\(_2\)) is produced at the positive electrode:

  \[ 4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4e^- \] (oxidation)

What happens during the electrolysis of sodium chloride (NaCl)?
Halides – an exception to the rule

Normally during the electrolysis of an aqueous solution, oxygen is produced at the positive electrode.

An exception to this rule is when a halide ion is present, for example chloride ions.

The chloride ions outcompete the hydroxide ions at the positive electrode. This results in the formation of chlorine gas.

What happens during the electrolysis of hydrochloric acid, HCl?
Electrolysis of NaCl solution

What are the products of the electrolysis of aqueous sodium chloride solution, NaCl?

- chlorine (Cl$_2$)
- hydrogen (H$_2$)
- sodium hydroxide (NaOH).

Are these products what you expected?

Why?
Electrolysis of NaCl solution
The negative electrode
Why is sodium not formed?

In the electrolysis of sodium chloride solution, the Na\(^+\) ions might be expected to form sodium at the negative electrode. Instead, **hydrogen gas** is produced.

This is because sodium chloride solution also contains H\(^+\) ions from the water:

\[ \text{H}_2\text{O} (l) \rightarrow \text{H}^+ (aq) + \text{OH}^- (aq). \]

At the negative electrode, H\(^+\) ions compete with Na\(^+\) ions. The H\(^+\) ions gain electrons, leaving the Na\(^+\) ions in solution.

For all aqueous ionic compounds containing a metal that is more reactive than hydrogen, electrolysis will produce hydrogen rather than the metal.
How does sodium hydroxide form?

Sodium chloride solution has four different ions:
- Na\(^+\) and Cl\(^-\) ions from the sodium chloride
- H\(^+\) and OH\(^-\) ions from the water.

The Cl\(^-\) ions outcompete OH\(^-\) ions at the positive electrode to form chlorine gas.

The H\(^+\) ions outcompete the Na\(^+\) ions at the negative electrode. This leaves Na\(^+\) and OH\(^-\) ions in solution, which form sodium hydroxide, NaOH.

What is the overall equation for the electrolysis of NaCl?

\[
2\text{NaCl (aq)} + 2\text{H}_2\text{O (l)} \rightarrow \text{H}_2 (g) + \text{Cl}_2 (g) + 2\text{NaOH (aq)}
\]
### Electrolysis products

**What are the products of these electrolysis reactions?**

<table>
<thead>
<tr>
<th>Ionic compound in solution</th>
<th>Product at anode (+)</th>
<th>Product at cathode (−)</th>
</tr>
</thead>
<tbody>
<tr>
<td>copper chloride</td>
<td>chlorine</td>
<td></td>
</tr>
<tr>
<td>sodium chloride</td>
<td></td>
<td></td>
</tr>
<tr>
<td>potassium bromide</td>
<td>bromine</td>
<td></td>
</tr>
<tr>
<td>silver bromide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>copper sulfate</td>
<td>oxygen</td>
<td></td>
</tr>
</tbody>
</table>

**hydrogen**
Electrolysis of copper sulfate
Electrolysis of copper sulfate

Copper sulfate solution can be electrolysed using two types of electrodes; **inert** graphite or **non-inert** copper.

Electrolysis using copper electrodes results in a change in mass of the electrodes.

The **positive copper ions** move towards the negative electrode where they gain electrons, forming solid copper.

\[ \text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s) \]

The **negative sulfate ions** move towards the positive electrode where they react with the copper in the electrode.

\[ \text{Cu} + \text{SO}_4^{2-}(aq) \rightarrow \text{Cu}^{2+} (aq) + \text{SO}_4^{2-} (aq) + 2e^- \]
Changing electrode mass

The copper in the positive electrode dissolves into the solution, forming copper ions which move towards the cathode and deposit as solid copper.

What would you see if you weighed the electrodes before and after electrolysis?

There is no net change in concentration of copper sulfate in solution. This means that the blue colour of solution remains.

What would happen to the colour of the solution if graphite electrodes were used?
Purifying copper

Electrolysis can be used to **purify** copper following extraction from it’s ore:

- An impure positive copper electrode is used with a pure negative copper electrode.
- A copper sulfate electrolyte solution is used.
- The copper from the impure positive electrode is extracted by electrolysis.
- Copper ions from the impure electrode move to the negative electrode where they deposit as solid copper.
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Fill in the gaps