

The Electrolysis process and its thermodynamic limits

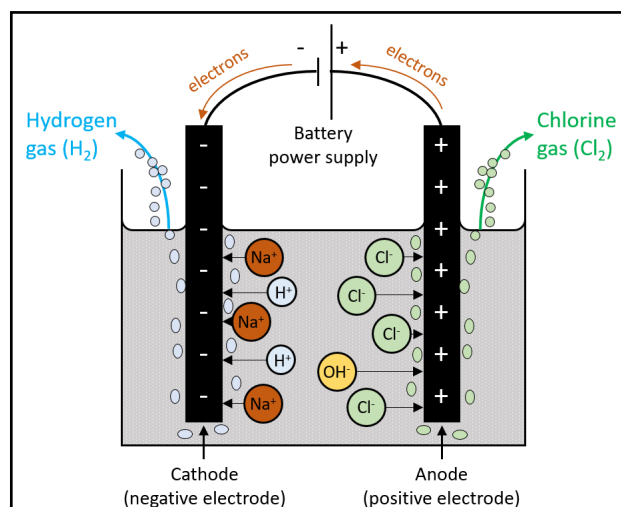
The production of chlorine and caustic soda (chlor-alkali) involves using an electrolytic method. Electrolysis uses an electric current to drive a chemical reaction which otherwise would not occur spontaneously. For example, when dissolving kitchen salt in water, there is no spontaneous formation of chlorine, this only happens once an electrical current is sent through the solution.

An electrolysis unit consists of 2 electrodes:

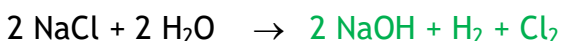
- 1) the anode, with a positive (+) charge
- 2) the cathode, with a negative (-) charge

The cathode attracts positive charges, whereas negative charges migrate towards the anode. Whether these migrations actually take place and how fast the movements will be, depends on the difference in voltage between both electrodes (the higher the difference, the faster the migration).

In chlor-alkali electrolysis units, chlorine gas is mostly produced from common, kitchen salt:



The principle of electrolysis starting from a brine (kitchen salt) solution

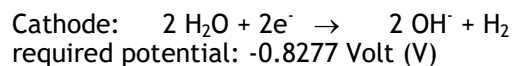
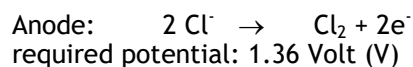


Kitchen salt + water → caustic soda + hydrogen gas + chlorine gas

To achieve this, brine (a highly concentrated salt solution in water, in this case NaCl) and water are brought into the system. The salt will dissolve in the water and split into Na⁺ and Cl⁻.

At the anode, pairs of negatively charged chloride (Cl⁻) ions transform into chlorine (Cl₂) by giving off two electrons. Cl₂, being a gas, will bubble from the solution and is subsequently collected. Meanwhile, at the cathode, hydrogen (H₂) gas forms as the water molecules scoop up the 2 electrons mentioned above.

To make these chemical transformations happen, each electrode needs to have a minimal voltage or 'potential':



This means that the energy source for this electrolysis unit (e.g. the local electricity supply) needs to ensure that the difference between these electrodes (i.e. 2.1877 V) is achieved. Using electrical laws, we can calculate the required amount of energy (expressed in kWh)

For 1 ton of Cl₂ plus 1.1282 ton of NaOH plus 28.4 kg H₂, one needs ... 1653.8 kWh





This means that a minimum energy demand of 1654 kWh / tonne Cl₂ is required to bring about the reactions, forming the required chemicals which store this energy in any product where this chlor-alkali ends up.

This means that, when one uses those products in other processes, the 1653.8 kWh potentially can (partly) be released again, depending on the efficiency of the reactions taking place. For example, when H₂ and Cl₂ react to produce gaseous HCl, a significant amount of energy (720 kWh) is released as heat, the reaction temperature being around 2500°C. This high temperature HCl gas still contains a lot of energy.

It should be noted that simply putting the thermodynamic minimum energy demand of 1654 kWh/ton Cl₂ into the system, will not lead to efficient chlorine production though.

There are several reasons for this:

- The mentioned voltage of 2.1877 Volt may be sufficient to allow the reactions to occur, but at much too slowly a rate. Usually between 2.5 and 3.5 Volt is needed to cause the electrons to move towards the electrodes at an acceptable speed and to give an efficient reaction rate at the electrodes.
- Once the reaction has occurred, the reaction products need to remain separated. Indeed, H₂ and Cl₂ can form an explosive gas mixture as well as forming HCl, whilst Cl₂ and NaOH will form NaClO (hypochlorite or 'bleach'). To separate them, a special membrane (or a 'diaphragm') is installed between both electrodes. Having this essential separation brings about a (small) drop in the voltage.
- Finally, whenever electrons travel through an electrical conducting system, there are slight losses (as heat). This will also be the case for the current taking care of the energy supply. No system is 100% efficient at carrying these electrons without small losses.

It is evident that more energy will be required than the amount of energy that is eventually stored in any chlor-alkali product. The following table gives an idea of the additional voltages:

Over-potential at the electrodes
0.10 - 0.27 Volt
Membrane/diaphragm
0.40 - 0.50 Volt
Losses in the conducting systems
0.05 - 0.10 Volt

TOTAL
0.55 - 0.87 Volt

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In terms of energy consumption, this results in an additional 416 - 658 kWh per tonne of chlorine.

It is self-evident that, when building more modern electrolysis units, engineers carefully weigh the reduction in energy losses versus the required reaction speed and continuously look into new technical developments to reduce the losses.

Next to the electric equipment aspects leading to **voltage losses**, there is one additional physical and one additional chemical aspect that need to be taken into account. The separation wall (membrane or diaphragm) is not 100% perfect, meaning that some OH⁻ molecules will manage to get through.

Some competing reactions may also occur on the anode:

- 1) Water may be transformed into oxygen, 'polluting' the chlorine gas:
 $2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$
- 2) OH⁻ that back-migrated from the cathode side via an imperfection in the membrane, may:
 - form hypochlorite or chlorate by reacting with chlorine
 - form water and oxygen as follows:
 $4 \text{OH}^- \rightarrow \text{O}_2 + 2 \text{H}_2\text{O} + 4\text{e}^-$

When these reactions occur, they are considered as a **loss of reaction efficiency**. Typical reaction efficiencies are in the range of 92% to 99%.

Taking everything together, it can be concluded that the total energy consumption when producing chlorine through the electrolysis process described earlier, consists of the following components:

Thermodynamic minimum	1654 kWh / tonne Cl ₂	(> 70%)
Voltage losses	416 - 658 kWh / tonne Cl ₂	(± 23%)
Efficiency losses	21 - 201 kWh / tonne Cl ₂	(± 5%)

TOTAL
2091 - 2513 kWh / tonne Cl₂

The improvements for energy saving will focus on developing better membranes (higher efficiency) and membranes with a lower voltage (lower energy consumption). Finally, the economic aspect needs consideration, meaning that any investment shall be weighed up against operational costs.

Much more about chlorine at www.eurochlor.org

Chlorine chemistry applications: www.chlorinethings.eu

