

Electrolysis and electrolytic conductivity

Electrolysis

This is the decomposition of an ionic compound in molten or solution form to its constituent elements.

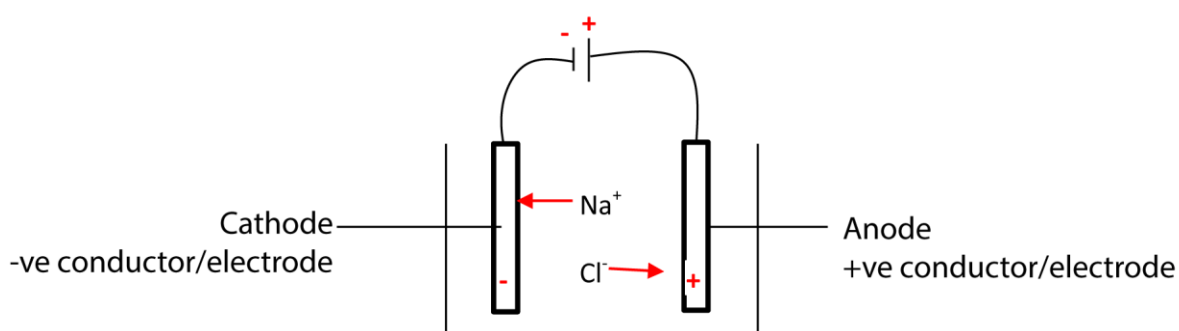
Mechanism of electrolysis

Consider electrolysis of molten sodium

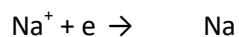
In molten form sodium chloride ionizes as follows



In an electrolytic cell, unlike charges attract; Na^+ migrate to the cathode while Cl^- migrate to the anode.



At the cathode, Na^+ ion acquires an electron to become sodium atom.



At the anode the Cl^- loses an electron to form a Cl atom



The chlorine atoms combine to form chlorine gas.

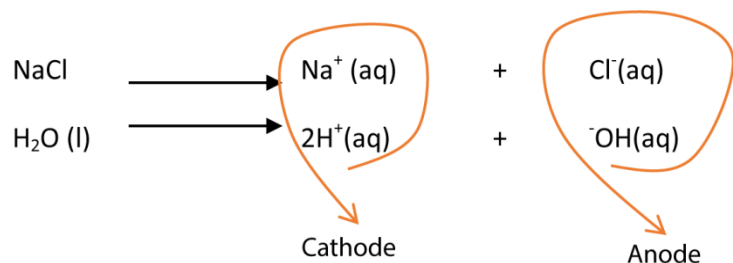


Ultimately, sodium chloride in molten form is decomposed by electrolysis to sodium metal and chlorine gas.

Selective discharge

Consider electrolysis of sodium chloride solution

Both sodium chloride and water ionize to form ions



The positively charged ion migrate to the cathode while negatively charged ions migrate to the anode.

Factors that decide the ion to be eliminated or discharged first.

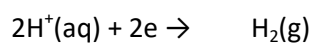
(i) **Position in electro-chemical series:**

Series for cations (**high to low**) K⁺, Ca²⁺, Na⁺, Mg²⁺, Al³⁺, [C], Zn²⁺, Fe²⁺, Pb²⁺, Cu²⁺, Ag⁺

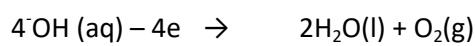
Series for anions (**high to low**) SO₄²⁻, NO₃⁻, Cl⁻, Br⁻, I⁻, -OH

The ion lower in electro-chemical series is discharged first. Consequently, during electrolysis of dilute sodium chloride, H⁺ which is low in the reactivity series than Na⁺ is discharged at the cathode whereas, OH⁻ ions are discharged at the anode.

At the cathode



At the anode

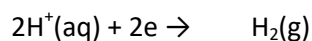


(ii) **Concentration:**

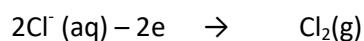
When Cl⁻, Br⁻ or I⁻ are concentrated, then they will be discharged with respect to OH⁻.

In this case electrolysis of concentrated sodium chloride solution liberates chlorine at the anode and hydrogen gas at the cathode (concentration does not affect Na⁺)

At the cathode



At the anode

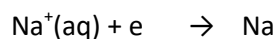


(iii) **Nature of electrode**

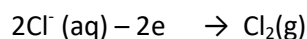
(a) When mercury cathode is used Na⁺ is discharged with preference to H⁺.

Therefore, electrolysis concentrated sodium chloride using mercury cathode liberates Na at the cathode and chlorine gas at the anode (due to high concentration of Cl⁻).

At the cathode



At the anode



Application of electrolysis

1. Industrial preparation of gases; Cl_2 , H_2 and O_2 .
2. Extraction of metal: metals above carbon in the reactivity series are almost all extracted by electrolysis.

Example Extraction of sodium.

Ore: molten NaCl

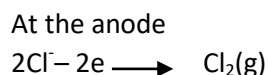
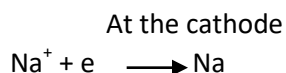
Anode: iron cylinder is cheap and has a melting point above the melting point of NaCl .

Cathode: carbon because it does not react with chloride.

Calcium chloride added to the mixture to

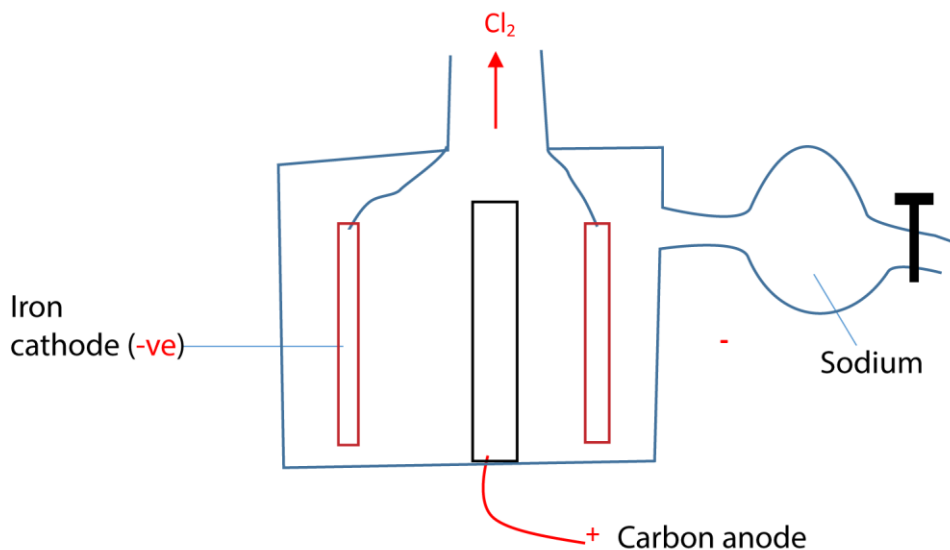
- lower the melting point of sodium chloride from 800°C to 600°C ,
- reduce solubility of sodium in molten sodium chloride,
- Lower the corrosive vapor of sodium chloride.

Sodium is collected in dry nitrogen to protecting it from reacting with air.



Setup

The setup is such chlorine produced does not react with sodium

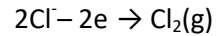


3. Preparation of sodium hydroxide

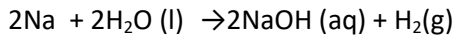
By electrolysis of concentrated solution of sodium chloride using carbon anode and mercury cathode. At the anode chlorine is liberated and at mercury cathode Na^+ instead of H^+ is discharged and dissolved in mercury to form mercury amalgam.

At the cathode

At the anode



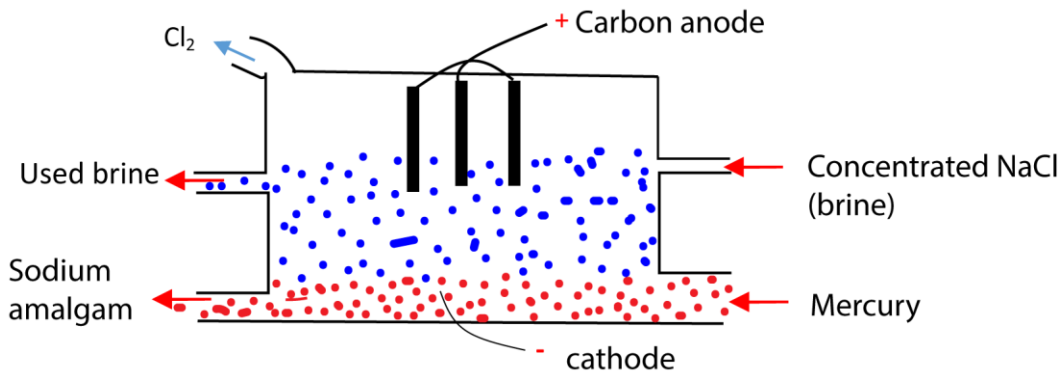
When sodium amalgam is dropped in water, sodium reacts to form sodium hydroxide and hydrogen gas.



Sodium hydroxide is concentrated to form pellets.

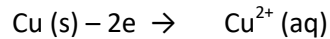
This process is disadvantageous because it releases poisonous mercury into the environment

Setup



4. Purification of copper

Anode: impure copper (dissolves)



Cathode (copper is deposited)



Electrolyte: copper sulphate solution

Copper migrated from the anode to the cathode.

Faraday's Laws of electrolysis

1. The mass of a substance liberated at an electrode is proportional to the quantity of electricity used.

The quantity of electricity Q in coulombs = It

(I = current of electricity in amperes, t = time in second)

2. The moles of electricity required to liberate one mole of an element is proportion to the charge on its ions. (1mol of electricity = 1Faraday = $1F = 96500 \text{ C}$)

Example

Calculate the mass of copper liberated by a current of 1A for 1hour. ($\text{Cu} = 63.5$)

Quantity of electricity $Q = It = 1 \times (1 \times 60 \times 60) = 3600\text{C}$



It implies that (96500 x2) C is required to liberate 63.5 g of copper

Therefore, 3600C will liberate $\frac{63.5 \times 3600}{2 \times 96500} = 1.18\text{g}$