

## Electrolytic cell

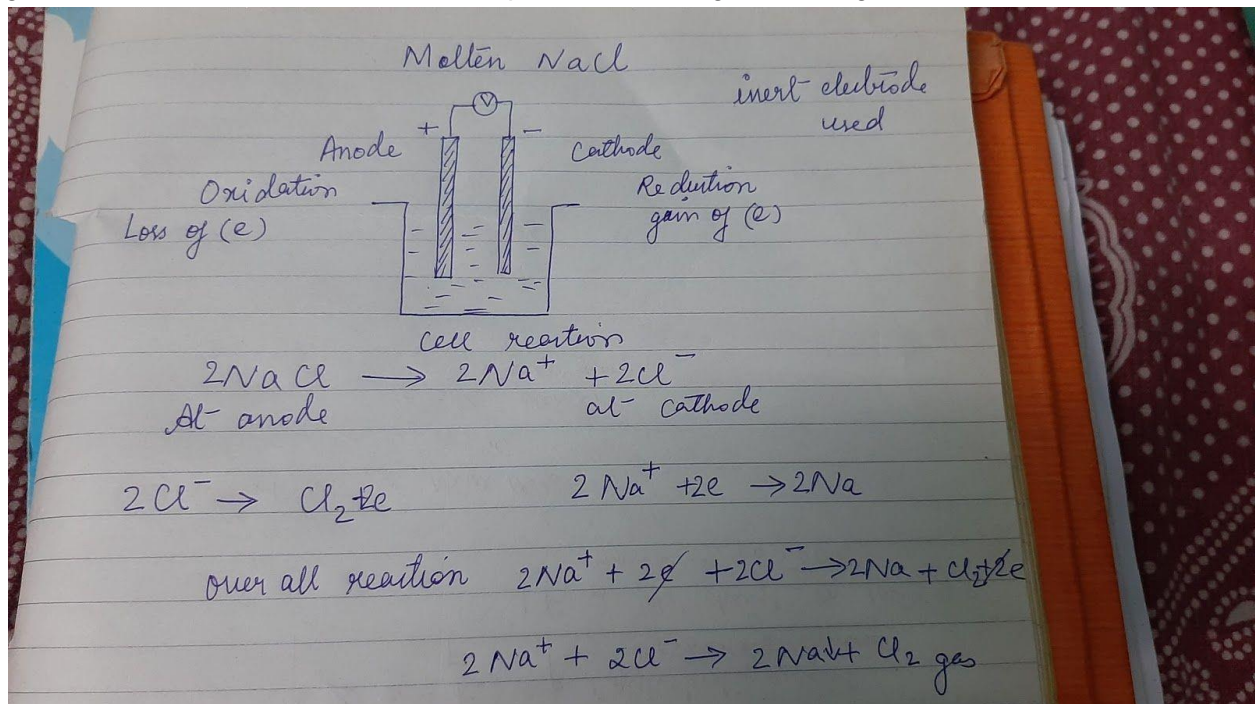
Electrolytic cell works on the principle of electrolysis. Electrolysis means to split the chemical using electrical energy, therefore in an electrolytic cell electrical energy converts into mechanical energy the cell reaction is non spontaneous, let's see how the electrolytic cell is constructed.

An electrolytic cell consists of a non conducting vessel, inside the vessel electrolytic solution is taken the electrolyte can be either in aqueous or in molten state two electrodes are used which helps to conduct electricity, they can be non reactive like graphite or Platinum these electrodes are called inert electrodes because they do not take part in the cell reaction. The Other electrode is the reactive electrode like Copper, zinc, silver they are reactive hence they take part in the cell reaction.

The cell reaction

Molten NaCl

The electrolyte in the state of molten NaCl will get deposited as sodium metal in cathode. The cell reaction are, at the anode the Anion  $\text{Cl}^-$  will donate the electron and discharge into chlorine gas. at the cathode the cation will accept electron and get discharged as sodium metal.

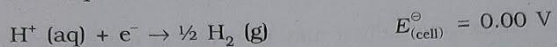
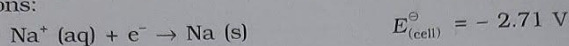


In case of aqueous electrolyte the situation will be different because four types of ions will be dissociated in solution they are sodium ion chloride ion hydrogen ion and Hydroxide ion hence there will be a competition which ion will be depositing at the anode and cathode The choice of deposition is done on the basis of standard reduction potential series

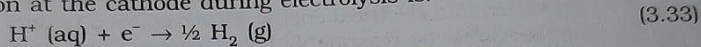
electrodes, the products present in the electrolytic cell and their standard electrode potentials. Moreover, some of the electrochemical processes although feasible, are so slow kinetically that at lower voltages these do not seem to take place and extra potential (called *overpotential*) has to be applied, which makes such process more difficult to occur.

For example, if we use molten NaCl, the products of electrolysis are sodium metal and Cl<sub>2</sub> gas. Here we have only one cation (Na<sup>+</sup>) which is reduced at the cathode (Na<sup>+</sup> + e<sup>-</sup> → Na) and one anion (Cl<sup>-</sup>) which is oxidised at the anode (Cl<sup>-</sup> → ½Cl<sub>2</sub> + e<sup>-</sup>). During the electrolysis of aqueous sodium chloride solution, the products are NaOH, Cl<sub>2</sub> and H<sub>2</sub>. In this case besides Na<sup>+</sup> and Cl<sup>-</sup> ions we also have H<sup>+</sup> and OH<sup>-</sup> ions along with the solvent molecules, H<sub>2</sub>O.

At the cathode there is competition between the following reduction reactions:



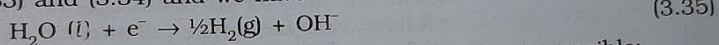
The reaction with higher value of  $E^{\ominus}$  is preferred and therefore, the reaction at the cathode during electrolysis is:



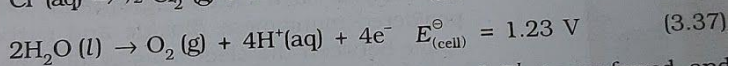
but H<sup>+</sup> (aq) is produced by the dissociation of H<sub>2</sub>O, i.e.,



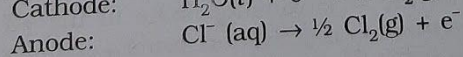
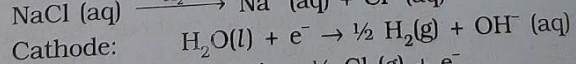
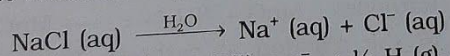
Therefore, the net reaction at the cathode may be written as the sum of (3.33) and (3.34) and we have



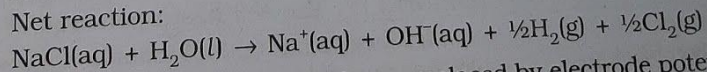
At the anode the following oxidation reactions are possible:



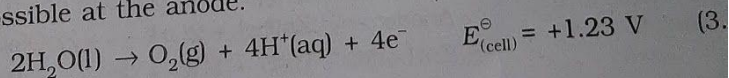
The reaction at anode with lower value of  $E^{\ominus}$  is preferred and therefore, water should get oxidised in preference to Cl<sup>-</sup> (aq). However in account of overpotential of oxygen, reaction (3.36) is preferred. Thus the net reactions may be summarised as:



Net reaction:



The standard electrode potentials are replaced by electrode potentials given by Nernst equation (Eq. 3.8) to take into account the concentration effects. During the electrolysis of sulphuric acid, the following process is possible at the anode:



Aq NaCl

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At anode	At cathode
$\text{Cl}^- / \text{OH}^-$	$\text{Na}^+ / \text{H}^+$
1.36V / 1.23V	-2.71 / 0.00V
$\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$	$\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$
1.36V > 1.23V	0.00 > -2.71

Hence  $\text{Cl}^-$  will get discharged  
 Hence  $\text{H}^+$  will get discharged.

At anode  $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e$

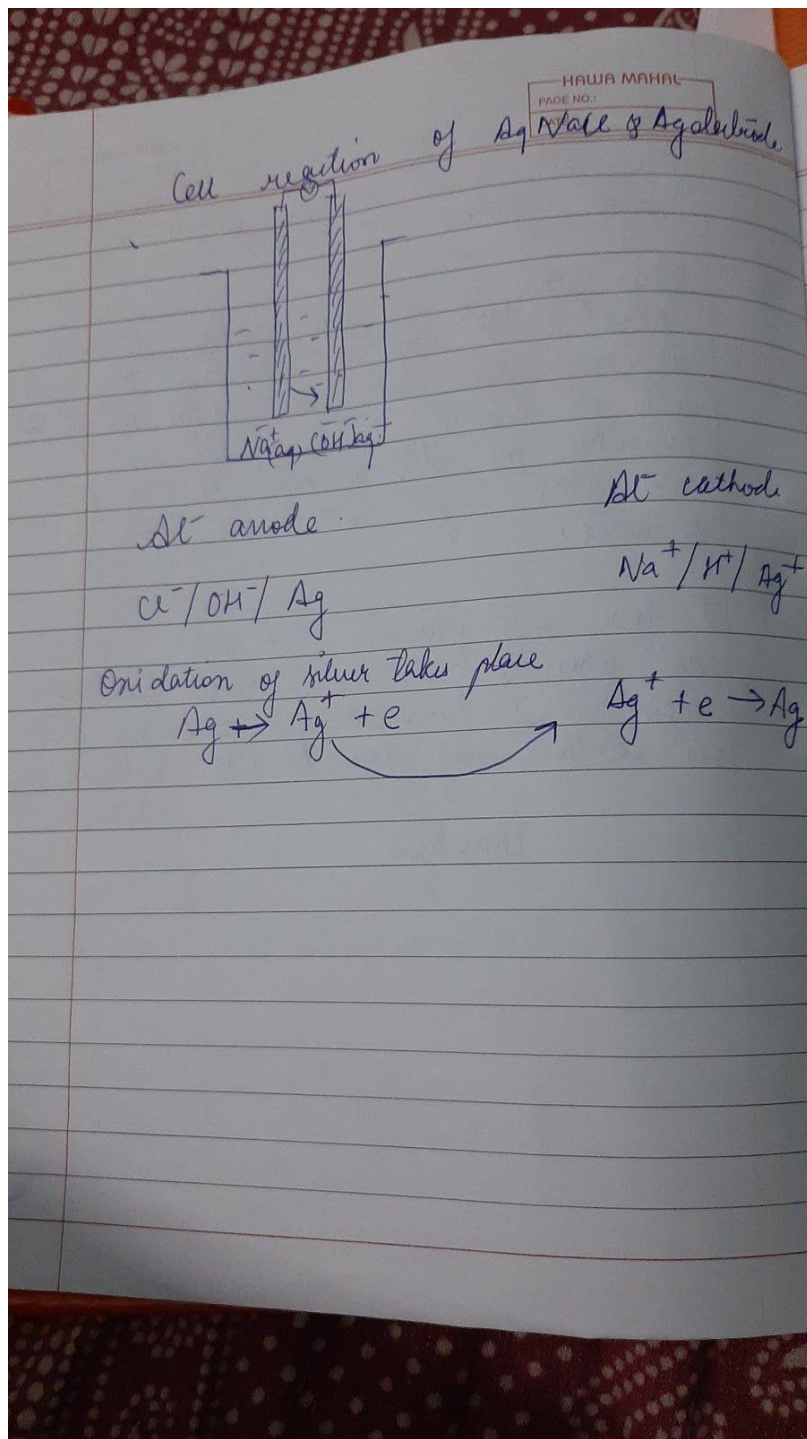
At cathode  $2\text{H}^+ + 2e \rightarrow \text{H}_2$

Over all reaction  $2\text{NaCl}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Na}^+(\text{aq}) + 2\text{OH}^-(\text{aq}) + \text{Cl}_2(\text{g}) + \text{H}_2(\text{g})$

If the electrodes are active then the electrodes will take part in the cell reaction. example of aqueous NaCl with silver electrodes if we take aq or molten NaCl with silver electrodes at anode and cathode, the active electrode reaction will take place. At cathode, silver is formed. At anode oxidation of silver takes place by the loss of electron. At cathode reduction of silver ion takes place by the gain of electron. this reaction is used for refining meta, I the anode is taken as impure metal and cathode as a pure metal when the

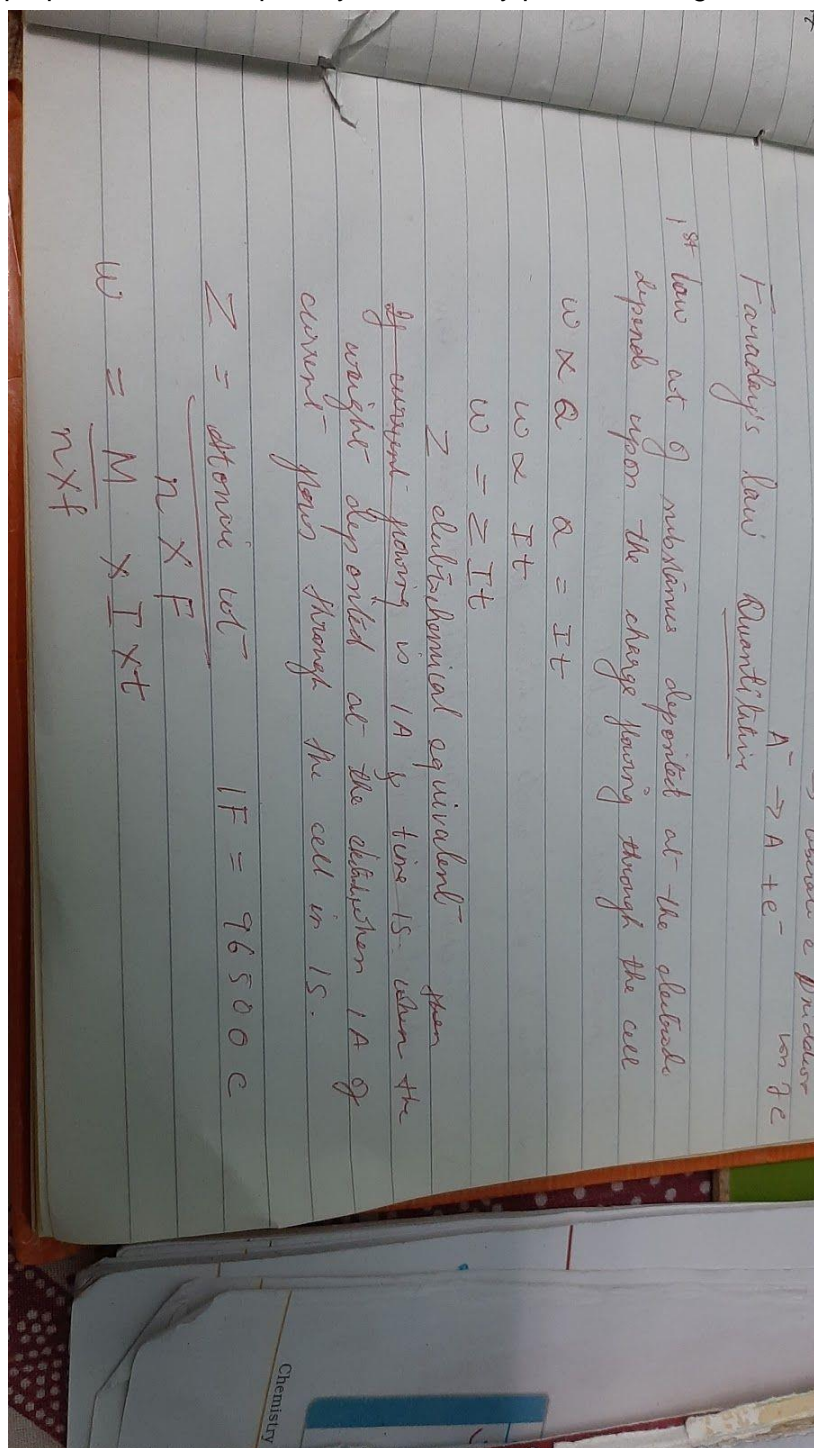


electrolysis is conducted the anode becomes thin and cathode will become thick showing that pure metal gets deposited at the cathode and metals from anode is been removed in the form of metal ion this method is also applied in electroplating of metals.



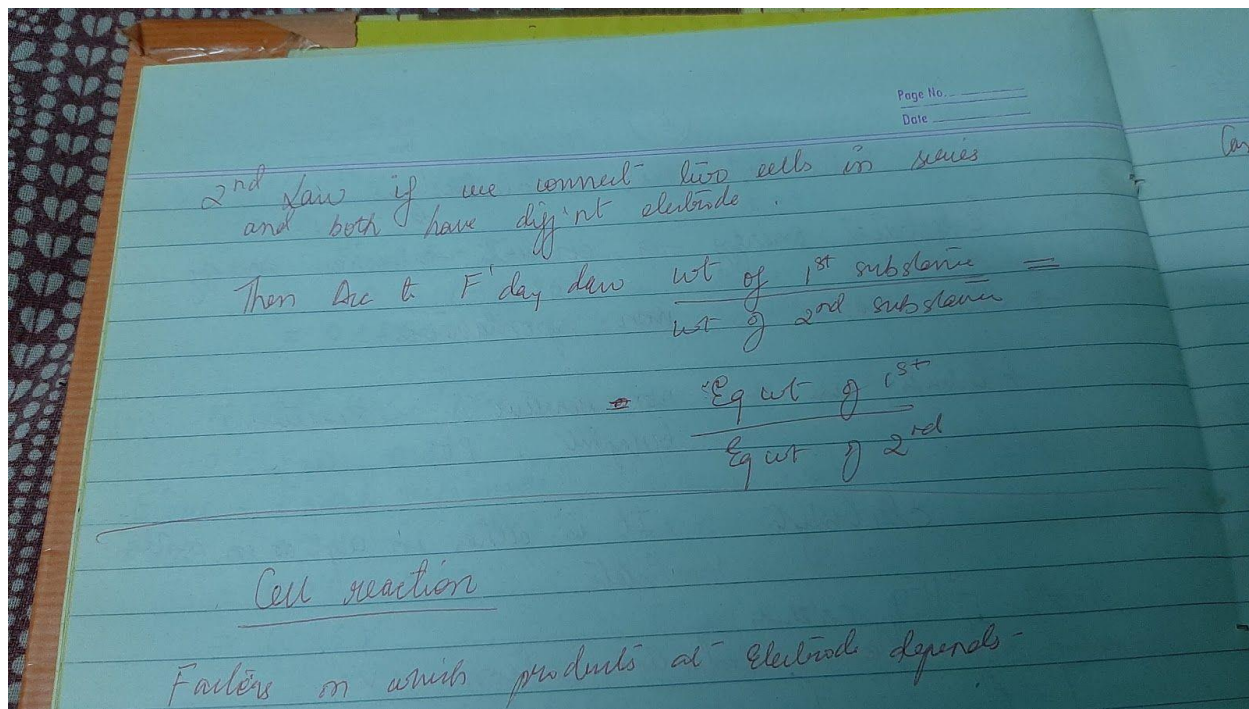
The quantitative aspect of electrolysis was given by Michael Faraday according to Faraday's two laws the electrolysis of the solution and it's melt of electrolyte was stated as:

1st law the amount of chemical reaction at the electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte



According to the second law the amount of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical Equivalent weight that is atomic mass of metal divided by number of electrons required to reduce the cation

In the second law if we connect two cells in series and both have different electrode then according to Faraday's law weight of first substance divided by weight of second substance will be equal to gram equivalent weight of first substance divided by gram equivalent weight of second substance.



Do in text questions on page 86.