

# CHEMISTRY STUDY MATERIALS FOR CLASS 12 (NCERT BASED NOTES OF CHAPTER -03)

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## Electrochemistry

### Electrolytic Cells and Electrolysis

In an electrolytic cell, the electrical energy is converted to chemical energy. The dissociation of an electrolyte by the passage of electricity is called electrolysis.

For e.g. when  $\text{CuSO}_4$  solution is electrolysed by Cu electrodes, Cu is deposited at the cathode and  $\text{Cu}^{2+}$  ions are liberated from the anode.

### Quantitative Aspects of electrolysis – Faraday's laws

#### 1) Faraday's first law

It states that the amount of substance deposited or liberated at the electrodes ( $m$ ) is directly proportional to the quantity of electricity ( $Q$ ) flowing through the electrolyte.

Mathematically,  $m \propto Q$

Or,  $m = zQ$

Where  $z$  is a constant called electrochemical equivalent (ECE).

$Z = \text{equivalent weight}/96500$

But quantity of electricity is the product of current in ampere ( $I$ ) and time in second ( $t$ ).

i.e.  $Q = It$  Therefore,  $m = zIt$

**1 Faraday** is the charge of 1 mole of electron or it is the amount of electricity required to deposit one gram equivalent of any substance. Its value is 96500 C/mol.

For the deposition of 1 mole of Na, the amount of charge required = 1 F (Since  $\text{Na}^+ + e^- \rightarrow \text{Na}$ )

For Ca,  $Q = 2F$  (since  $\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}$ )

#### 2) Faraday's second law

It states that *when same quantity of electricity is passed through solutions of different substances, the amount of substance deposited or liberated is directly proportional to their chemical equivalence.*

For e.g. when same quantity of electricity is passed through solutions of two electrolytes A and B, then

Mass of A deposited = Equivalent mass of A

Mass of B deposited = Equivalent mass of B

### Products of electrolysis

The products of electrolysis depend on the following factors:

i) *The nature of the electrolyte:* The electrolyte may be in molten state or in aqueous solution state.

e.g. if molten NaCl is electrolysed, Na is deposited at the cathode and chlorine is liberated at the anode.



At cathode:  $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$

At anode:  $\text{Cl}^- \rightarrow \frac{1}{2}\text{Cl}_2 + \text{e}^-$

If NaCl solution is electrolysed, we get  $\text{H}_2$  gas at the cathode and  $\text{Cl}_2$  gas at the anode.

NaCl solution contains 4 ions –  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{H}^+$  and  $\text{OH}^-$

Cathode reaction:  $\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2$

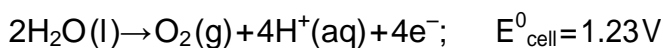
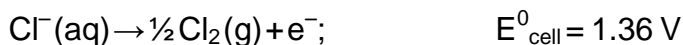
Anode reaction:  $\text{Cl}^- \rightarrow \frac{1}{2}\text{Cl}_2 + \text{e}^-$

NaOH is formed in the solution.

ii) *The type of electrodes used:* If the electrode is inert (e.g. Pt, gold, graphite etc.), it does not participate in the electrode reaction. While if the electrode is reactive, it also participates in the electrode reaction.

iii) *The different oxidising and reducing species present in the electrolytic cell and their standard electrode potentials.* Some of the electrochemical processes are very slow and they do not take place at lower voltages. So some extra potential (called *over potential*) has to be applied, which makes such process more difficult to occur.

For e.g. during the electrolysis of NaCl solution, the possible reactions at anode are:



At anode, the reaction with lower value of  $E^0_{\text{cell}}$  is preferred and so water should get oxidised in preference to  $\text{Cl}^-$  (aq). However, on account of over potential of oxygen, the first reaction is preferred and hence  $\text{Cl}_2$  is formed at anode.

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