Case II

Electrolysis of aqueous salts

a) Electrolysis of aqueous NaCl (conc.) using Pt electrodes

Ions present : Na^+, Cl^-, H^+, OH^-
H_2O

Ions at anode (oxidation)
Cl^-, OH^-

Cathode (reduction)
Na^+, H^+

Specie having higher oxidation potential is oxidised at anode

Specie having higher reduction potential is reduced at cathode

Anode reaction:

Li
K
Na
Zn
Fe
H
Cu
Ag
Cl^-
OH^-
NO_3^-
SO_4^{2-}
F^-

SRP ↑ SOP ↓

Cl^- gets oxidised

$2Cl^- \rightarrow Cl_2 + 2e^-$

Cathode reaction:

$2H^+ + 2e^- \rightarrow H_2$

Net reaction

$2Cl^- + 2H^+ \rightarrow Cl_2 + H_2$

Spectator ions: $2Na^+ + 2OH^-$ $\rightarrow$ $2Na^+ + 2OH^-$

(overvoltage)

$2NaCl + 2H_2O \rightarrow Cl_2 + H_2 + 2NaOH$

b) Electrolysis of dil NaCl

Ions present : Na^+, Cl^-, H^+, OH^-
H_2O

Ions present at anode (+ electrode)
Cl^-, OH^-

Ions present at cathode (-ve electrode)
Na^+, H^+

Reaction at anode (oxidation)

$2Cl^- \rightarrow Cl_2(g) + 2e^-$ $\quad E^\circ_{Cl^-/Cl_2} = -1.36\,V$

$2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$ $\quad E^\circ_{OH^-/O_2} = -1.23\,V$

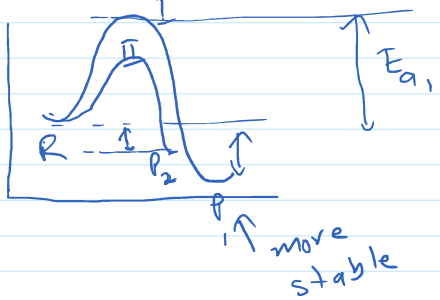
Reaction at cathode (reduction)

$2H^+ + 2e^- \rightarrow H_2$

Concept of overvoltage:

Some reactions of electrochemical process although feasible

are so slow kinetically that at lower voltages, these do not seem to take place and extra potential (over voltage) has to be supplied.



Net reaction

$$2H^+ + 2OH^- \rightarrow \frac{1}{2}O_2 + H_2 + H_2O$$

$$2H_2O \rightarrow \frac{1}{2}O_2 + H_2 + H_2O$$

$$H_2O \rightarrow \frac{1}{2}O_2 + H_2$$

This is case of electrolysis of water

c) Electrolysis of NaCl using Hg as cathode

Ions present: Na^+, Cl^-, H^+, OH^-

Ions present at anode (+ve terminal)

Cl^-, OH^-

Ions present at cathode (-ve terminal)

Na^+, H^+

Reaction at anode:

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

Reaction at cathode

$$Na^+ + e^- \rightarrow Na(s) \quad \checkmark$$

$$Na(s) + Hg \rightarrow Na.Hg \quad \checkmark$$

(sodium amalgam)

Due to high solubility of sodium in mercury and formation of sodium amalgam Na^+ gets preference over H^+ for reduction.

d) Electrolysis of NaCl(aq) using silver electrodes

Ions present: Na^+, Cl^-, OH^-, H^+

H_2O

Species at anode.

Species at cathode

H_2O

Species at anode. (+ve terminal)

Cl^-, OH^-, Ag

Species at cathode (-ve terminal)

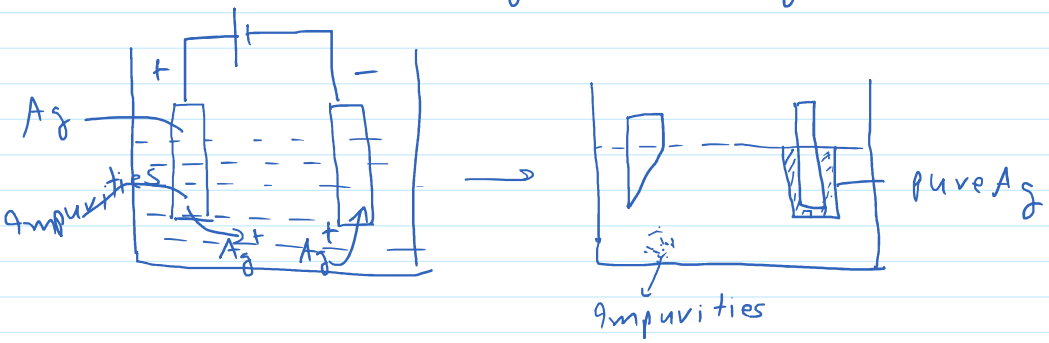
Na^+, H^+, Ag^+

Reaction at anode (oxidation)

$Ag \rightarrow Ag^+ + e^-$

Reaction at cathode

$Ag^+ + e^- \rightarrow Ag$.



Electrorefining → cathode Ag

Electroplating → cathode Cu.