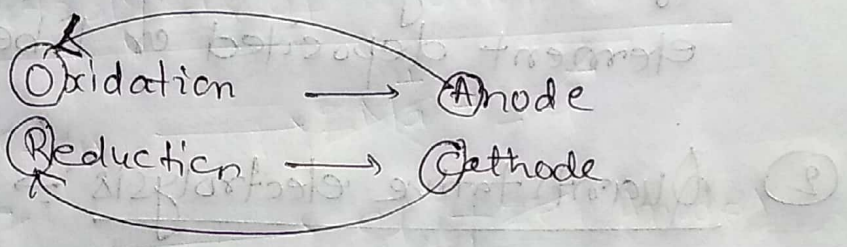
Electrochemistry (Lecture-3)

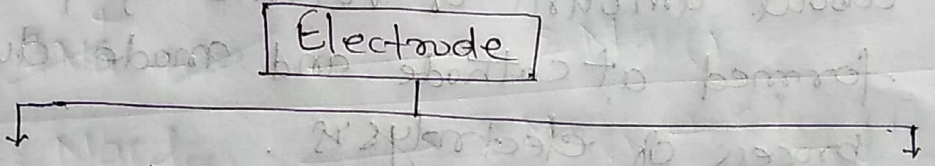
Electrolytic cell

→ It consist two electrode and one electrolyte.

Anode :→ Metal strip at which oxidation occur called anode.
→ Current enters through it.
→ It is positively charge.

Cathode :→ Electrode through which current leaves.
→ Reduction occurs at cathode.
→ It is negatively charged.





Active electrode
or
Attackable electrode

→ It participate in electrode reaction.
→ Made up of reactive metals.
→ Get oxidised and their mass decreases
e.g:- Zn, Cu, Ag, Hg

Inactive electrode
or
Non-attackable electrode

→ It donot pasticipate in electrode reaction.
→ Made up of non-reactive metal.
→ They do not dissolved and their mass remain same.
→ It acts as source or sink of electrons.
e.g:- Au, Pt etc.

Electrolysis

→ Process of decomposition of compound by passing electricity through its molten state or aqueous solution.

It is of two types:-

(1) Qualitative electrolysis :→ Study of nature of possible products formed at anode or cathode in the process of electrolysis. i.e which type of element deposited or liberated.

(2) Quantitative electrolysis :→ It deals about amount or volume of products formed at cathode and anode during process of electrolysis.

Electrochemistry (Lecture-4)

Factors affecting products of electrolysis

1. Electrode potential of reaction at cathode or anode (deposition or liberation)
2. Concentration of the ions in the solution.
3. Types of electrode (Reacting or non reacting)
4. Over potential of gases with respect to electrode.

(a) Electrolysis of molten NaCl

$$2NaCl(s) \longrightarrow 2Na^{+} + 2Cl^{-}$$

$$2Cl^{-} \longrightarrow Cl_2(g) + 2e \quad \text{(Anode)}$$

$$2Na^{+} + 2e \longrightarrow 2Na(s) \quad \text{(cathode)}$$

$$2NaCl(s) \longrightarrow 2Na(s) + Cl_2(g)$$

(b) Electrolysis of molten $MgCl_2$

$$MgCl_2(s) \longrightarrow Mg^{2+} + 2Cl^{-}$$

$$2Cl^{-} \longrightarrow Cl_2(g) + 2e \quad \text{(Anode)}$$

$$Mg^{2+} + 2e \longrightarrow Mg(s) \quad \text{(cathode)}$$

$$MgCl_2(s) \longrightarrow Mg(s) + Cl_2(g)$$

© Electrolysis of molten K_2SO_4

$[K_2SO_4 \longrightarrow 2K^+ + SO_4^{2-}]$

$2SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2e$ (Anode)

(Peroxodisulphate)

$2K^+ + 2e \longrightarrow 2K_{(s)}$ (cathode)

$2K^+ + 2SO_4^{2-} \longrightarrow 2K_{(s)} + S_2O_8^{2-}$

(d) Electrolysis of molten $Na_2S_2O_3$

$[Na_2S_2O_3 \longrightarrow 2Na^+ + S_2O_3^{2-}]$

$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e$ (Anode)

(Tetrathionate ion)

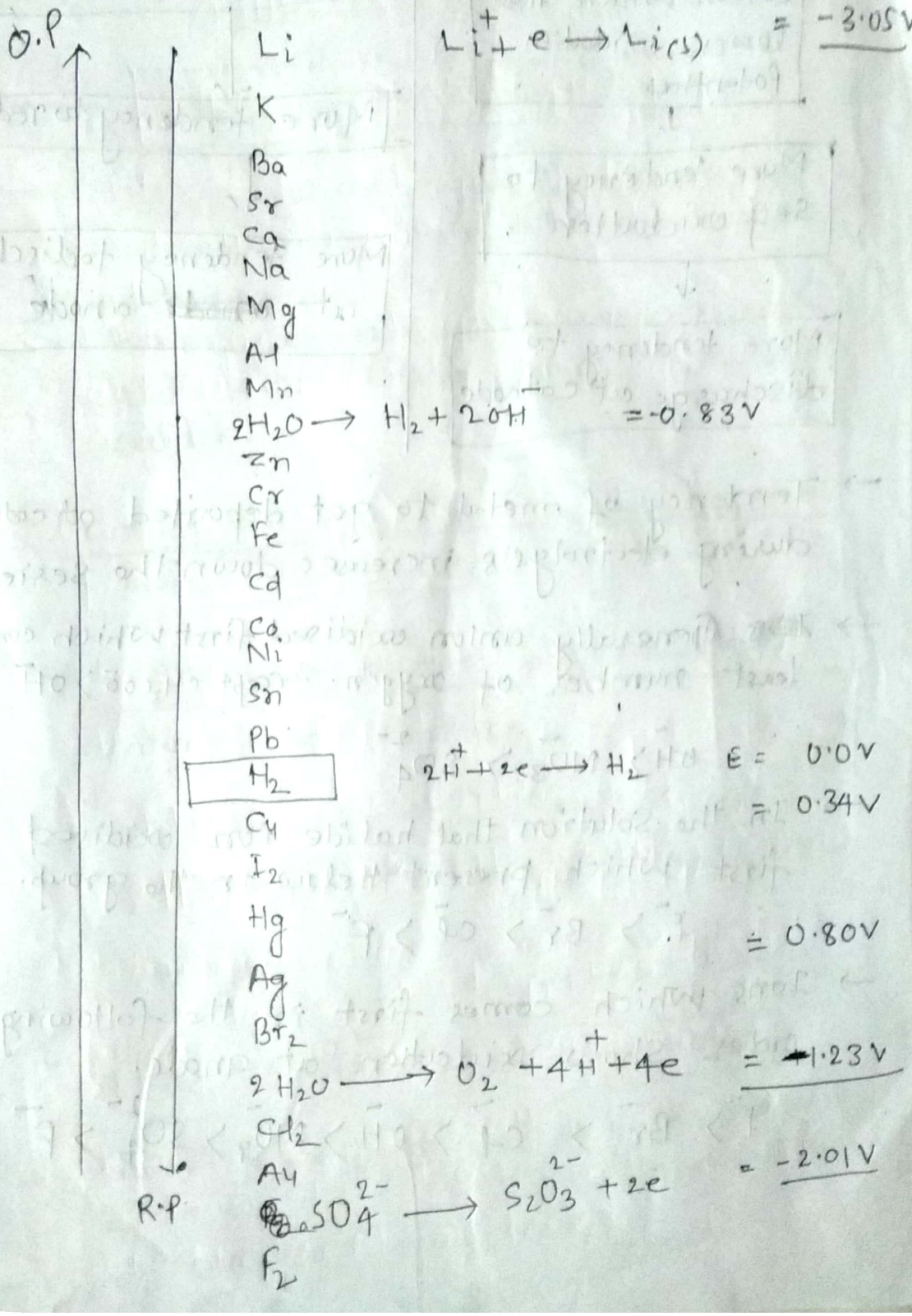
$2Na^+ + 2e \longrightarrow 2Na_{(s)}$ (cathode)

$2Na^+ + 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2Na_{(s)}$

Electrochemistry (Lecture-6)

Electrochemical Series

→ Those series in which elements are arranged in increasing order of their standard reduction potential is called electrochemical series.



Among two cations

↓

Cation which has higher Reduction Potential.

↓

Cation which has lower oxidation Potential.

↓

More tendency to self oxidation

↓

More tendency to discharge at cathode

Among two anions

↓

Anions which has higher oxidation potential

↓

Anions which has lower reduction potential

↓

More tendency to reduction

↓

More tendency to discharge at anode

→ Tendency of metal to get deposited at cathode during electrolysis increases down the series.

→ Generally anion oxidised first which contain least number of oxygen. except $CH_3COO^- > OH^-$

$$OH^- > NO_3^- > SO_4^{2-}$$

→ In the solution that halide ion oxidised first which present below in the group.

$$I^- > Br^- > Cl^- > F^-$$

→ Ions which comes first in the following order show oxidation at anode.

$$I^- > Br^- > Cl^- > OH^- > NO_3^- > SO_4^{2-} > F^-$$

Electrochemistry (Lecture-7)

Electrolysis of water (Aqueous solution)

At cathode (Reduction of cation)

$$2H^+ + 2e \longrightarrow H_2$$

$$\boxed{2H_2O + 2e \longrightarrow H_2 + 2OH^-}$$

At anode (Oxidation of anion)

$$4OH^- \longrightarrow O_2 + 2H_2O + 4e$$

$$\boxed{2H_2O \longrightarrow O_2 + 4H^+ + 4e}$$

→ Water reduced to give hydrogen gas and OH^- ion hence solution become alkaline.

→ Water oxidise to give oxygen gas and H^+ ion hence solution becomes acidic.

* Concentration of ions in solution affect products on electrode :-

(A) Electrolysis of aqueous NaCl (concentrated)

→ Using inert electrode.

$$2NaCl \longrightarrow 2Na^+_{(aq)} + 2Cl^-_{(aq)}$$

$$2H_2O + 2e \longrightarrow H_{2(g)} + 2OH^-_{(aq)} \quad \text{(cathode)}$$

$$2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2e \quad \text{(Anode)}$$

$$2NaCl + 2H_2O \longrightarrow 2Na^+ + 2OH^- + H_2 + Cl_2$$

→ Water needs greater voltage for oxidation to O_2 because it is slow process than oxidation of chloride (Cl^-) ions to Cl_2.

(B) Electrolysis of aqueous NaCl (very dilute)

→ Using inert electrode -

At cathode :-

$$2H_2O_{(l)} + 2e \longrightarrow H_{2(g)} + 2OH^-_{(aq)} \text{ (cathode)}$$

At anode :-

$$2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$$

* When NaCl is highly dilute, there is a very less chance of chloride (Cl^-) getting oxidised due to less number of chloride (Cl^-). So water (H_2O) will get oxidised.

(C) Electrolysis of aqueous NaCl solution

→ Using Mercury (Hg) electrode or active electrode.

At cathode :-

$$Na^+_{(aq)} + e \longrightarrow Na_{(s)}$$

At ~~cathode~~ anode :-

$$2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2e$$

→ When Hg electrode used then sodium deposited at cathode to form sodium amalgam.

$$Na_{(s)} + Hg_{(s)} \longrightarrow NaHg_{(s)}$$

(D) Electrolysis of aq. $CuSO_4$ solution (using Cu electrode)

At cathode

$$Cu^{2+}_{(aq)} + 2e \longrightarrow Cu_{(s)} \text{ (cathode)}$$

At anode

$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e \text{ (anode)}$$

(E) Electrolysis of aqueous Na_2SO_4 (Using inert electrode)

At anode

$$2H_2O(l) \longrightarrow O_2(g) + 4H^+_{(aq)}$$

At cathode

$$2H_2O(l) + 2e \longrightarrow H_2(g) + 2OH^-$$

(F) Electrolysis of aqueous H_2SO_4 solution (dilute)

→ Using inert electrode.

At anode :-

$$2H_2O(l) \longrightarrow O_2(g) + 4H^+_{(aq)} + 4e$$

At cathode

$$2H_2O(l) + 2e \longrightarrow H_2(g) + 2OH^-_{(aq)}$$

(G) Electrolysis of aqueous ~~solution~~ $AgNO_3$ solution.

→ Using active electrode Ag.

$$AgNO_3 \longrightarrow Ag^+ + NO_3^-$$

At cathode :-

$$Ag^+_{(aq)} + e \longrightarrow Ag(s)$$

At anode

$$Ag(s) \longrightarrow Ag^+ + e$$

* concentration of Ag^+ in the solution remain constant during electrolysis.

(H) Electrolysis of aqueous $NiSO_4$ solution

→ Using inert electrode.

At anode

$$2H_2O(l) \longrightarrow O_2(g) + 4H^+_{(aq)} + 4e$$

At cathode

$$Ni^{2+}_{(aq)} + 2e \longrightarrow Ni(s)$$