{Hydrogen potential = 0}

Anode ma hune rxn → Anode half rxn
cathode ma huni rxn → cathode half rxn
Duitai ma huni rxn → Net rxn

$E^0_{Zn^{++}/Zn} = -0.77V$
$E^0_{Cu^{++}/Cu} = 0.34V$

↳ cell notation:- Anode / solution of Anode // solution of cathode / cathode

* Zn-Cu voltaic cell (Daniel cell)
[$E^0_{Zn^{++}/Zn} = -0.77V$.
$E^0_{Cu^{++}/Cu} = 0.34 V$
→ Standard reduction potential of Zn is less than that of Cu. Therefore Zn is made anode whereas Cu is made cathode.

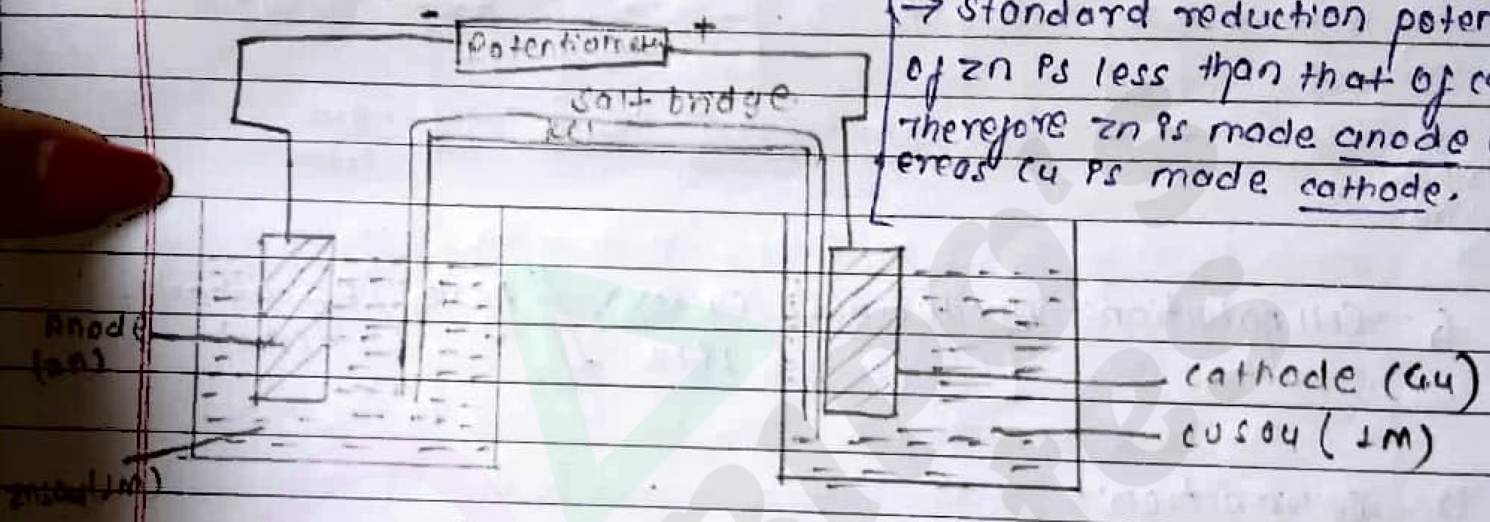


fig:- Daniel cell

↳ cell notation : $Zn / \underset{1M}{ZnSO_4}$ // cathode / $\underset{(1M)}{CuSO_4}$ / Cu.

↳ cell Reaction:-

① Anode half Reaction:- $Zn \longrightarrow Zn^{++} + 2e^-$

② ~~cat~~ cathode half Reaction:- ~~Cu++ + 2e~~ $Cu^{++} + 2e^- \rightarrow Cu$

③ Net Reaction:- $Zn + Cu^{++} \longrightarrow Zn^{++} + Cu$.

Table → Afu → reduce. Atu → oxidise | Mathi ko → anode due to oxidation (low) value. Tala ko → cathode due to Reduction (high) value

~~Standard~~ ↳ all for Reduction Potential and oxi - reverse.

(4) To determine anode and cathod in galvanic cell (electro chemical cell):-

electrodes having lower reduction potential gets easily oxidised. Hence, it becomes anode. similarly, electrodes having higher lower potential gets easily reduce. Hence, it becomes cathode.

for eg:- ~~Zn~~ In, Zn - Cu galvanic cell

$Zn \longrightarrow Zn^{++} + 2e^-$ $E^o_{Zn^{++}/Zn} = -0.77V$ (anode)

$Cu^{++} + 2e^- \longrightarrow Cu.$ $E^o_{Cu^{++}/Cu} = 0.34V$ (cathode)

(5) To calculate emf of cell :-

standard emf of cell is calculated from following relation:-

$$E^o = E^o_{cathode} - E^o_{anode}$$

~~$E^o = E^o_{red} - E^o$~~ $E^o = E^o_{right} - E^o_{left}.$

(6) To predict whether a cell reaction is spontaneous or not:-

If emf of cell reaction is positive then the cell reaction is ~~[illegible]~~ feasible or spontaneous. similarly if the emf of cell reaction is negative then the cell reaction is non-spontaneous

Date:- 2078/12/23.
Day :- Wednesday.

PAGE NO.:
DATE: / /

~~Nerst Equation~~

* Nerst Equation
(To calculate emf of cell other than standard condition)

For general reduction reaction;

$$M^{n+} + ne^- \longrightarrow M$$

Reduction potential given by

$$E = E^0 - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

$$Or,\ E = E^0 - 2.303 \frac{RT}{nF} \log \frac{[M]}{[M^{n+}]}$$

At 25°C

$$E = E^0 - \frac{0.059}{n} \log \frac{M}{[M^{n+}]}$$

Q. What will be the electrode potential of Cu (copper) electrode when copper rod is emerged in decimolal concentration of $CuSO_4$ solution at 20°C? [Given: electrode potential of copper is 0.34V]

Given Temprature T = 20° = 293 K.
Electrode potential of copper is $(E^0_{Cu^{++}/Cu}) = 0.34$ V.
concentration of $[Cu^{++}] = 0.1$ M.
concentration of Cu is orbitorily taken as 1.

$$Cu^{++} + 2e \longrightarrow Cu$$

$$E = E^0_{Cu^{++}/Cu} - 2.303 \frac{RT}{nF} \log \frac{[Cu]}{[Cu^{++}]}$$

$$= 0.34 - \frac{2.303 \times 8.314 \times 293}{2 \times 96500} \log \frac{1}{0.1}$$

$$= 0.31 \times 1$$

$$= 0.31\ V$$

16th Chaitra, 2078.

* Calomel Electrode:-

Calomel electrode is a common form of secondary reference electrode which is based on reaction between mercury and mercurious chloride (Hg_2Cl_2).

It consist of glass tube which contains Hg at bottom over which a mixture of Hg and Hg_2Cl_2 is kept and above this the tube is filled with saturated KCl solution. Platinum wire is used for electrical contact. KCl solution act as salt bridge.

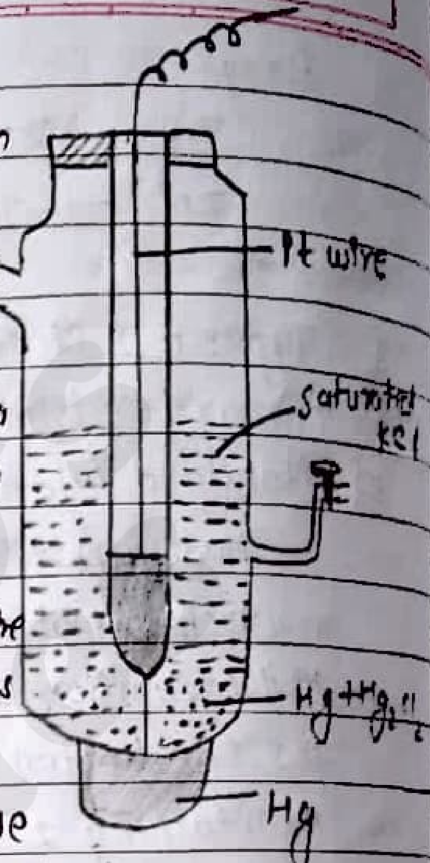


fig:- Calomel electrode

When calomel electrode act as anode then the electrode reaction is;

$$2Hg(l) \longrightarrow Hg_2^{2+} + 2e^-$$
$$Hg_2^{2+} + 2Cl^- \longrightarrow Hg_2Cl_2$$
$$2Hg(l) + 2Cl^- \longrightarrow Hg_2O_2 + 2e^- \text{ (oxidation)}$$

Similarly,

When it act as cathode the electrode reaction is:

$$Hg_2Cl_2 \longrightarrow Hg_2^{2+} + 2Cl^-$$
$$Hg_2^{2+} + 2e^- \longrightarrow 2Hg(l)$$
$$Hg_2Cl_2 + 2e^- \longrightarrow 2Hg(l) + 2Cl^- \text{ (Reduction)}.$$

* ~~cell reaction~~ cell reaction:-

↳ Oxidation half reaction:

$$Zn \longrightarrow Zn^{++} + 2e^-$$

↳ Reduction half reaction:-

$$Cu^{++} + 2e \longrightarrow Cu.$$

↳ Net reaction: $Zn / Cu^{++} \longrightarrow Cu + Zn^{++}$.

↳ Cell notation:- $Zn / Zn^{++} // Cu^{++} / Cu$.

* Can a solution of 1 M $CuSO_4$ solution be store in a vessel made of nickel. $\left[E^0_{Ni^{2+}/Ni} = -0.25V, \; E^0_{Cu^{2+}/Cu} = 0.34 \; V. \right]$

→ Here

Standard reduction potential of Nickel is less than that of copper. So, nickel lies above copper in electrochemical series. Since metal lying above in electrochemical series can displaces other metal lying below in electrochemical series from their salt solution. Therefore nickel displace copper from $CuSO_4$ solution. Hence $CuSO_4$ cannot be store in a vessel made of nickel.

* Predict which one of the following reaction is feasible? (possible)

① $2Fe^{++} + Sn^{4+} \longrightarrow 2Fe^{3+} + Sn^{++}$

② $2Fe^{3+} + Sn^{++} \longrightarrow 2Fe^{++} + Sn^{4+}$

Given →

$$E^0_{Fe^{3+}/Fe^{2+}} = +0.77V$$

$$E^0_{Sn^{4+}/Sn^{2+}} = 0.15 V.$$

Oxd. P → $E^\circ_{anode} + E^\circ_{cathode}$.

Red. P → $E^\circ_{cathode} - E^\circ_{anode}$

Red → electron accept.

Oxd → electron loss.

PAGE NO.:

DATE: / /

* EMF of cell:-

↳ $E^\circ = E^\circ_{cathode} - E^\circ_{anode}$ (taking reduction potential on both anode & cathode)

eg:- $- E^\circ_{Zn^{++}/Zn}$.

↳ $E^\circ = E^\circ_{anode} + E^\circ_{cathode}$ (if reduction potential of cathode & oxidation potential of anode is taken)

* Free energy change & Emf:-

$\Delta G = -nEF$

$\Delta G^\circ = nE^\circ F$

where n = no. of electrons involved in redox reaction.

E° = cell potential.

F = faraday's constant (96500 C).

* Calculate emf of a galvanic cell prepared from zinc and copper redox couples. The standard oxidation potential of zinc is + 0.76 V and s. Reduction potential of copper is + 0.34 V also write cell reaction and cell notation.

given →

$E^\circ_{Zn/Zn^{++}} = 0.76\,v.$, $E^\circ_{Zn^{++}/Zn} = -0.76\,v.$

$E^\circ_{Cu^{++}/Cu} = 0.34\,V.$

Here

$E^\circ_{Zn^{++}/Zn} < E^\circ_{Cu^{++}/Cu}$. Therefore Zn is made anode where Cu is made cathode.

$Emf = E^\circ_{cathode} - E^\circ_{anode}$

$= 0.34 - (-0.76)$

$= 1.10\,V.$

* **fuel cell:-** fuel cell is a device that convert the chemical energy of fuel directly into electrical energy by electrochemical reaction. It can supply electrical energy for long period of time since fuel and air is continuously supplied from an external source.

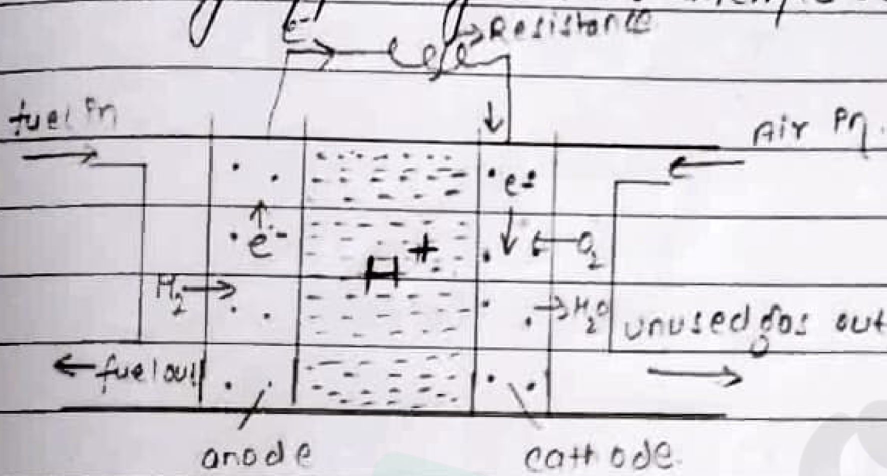


fig:- fuel cell.

* **Mechanism of fuel cell:-**

Fuel (hydrogen or reformed hydrogen) under go oxidation at anode and release electrones. These electrons flow through the external circuit to the cathode. At cathode O_2 from air get reduced. The electrons produce electricity while passing through external circuit. Electricity is generated as long as fuel and oxygen are supply to the electrodes.

At anode:-

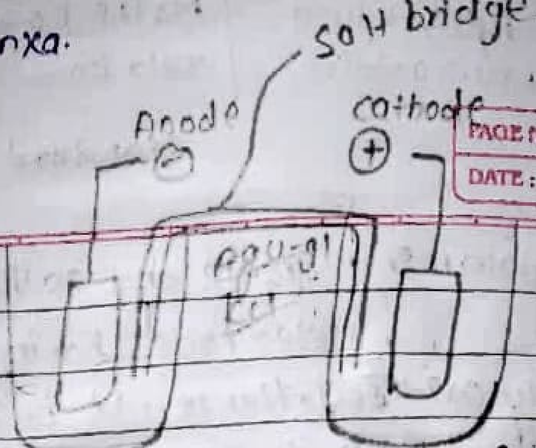
$$H_2 \longrightarrow 2H^+ + 2e^-$$

At cathode:-

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O.$$

salt-bridge ko conc :- high hunxa.

~~transport:- movility~~



* **Salt Bridge:-**

Salt Bridge is U-shaped tube containing ~~inner~~ inert electrolyte such as:- KCl, ~~NaN~~ KNO_3, Agar-Agar gel (Agu-gl). It helps to complete the internal circuit of galvanic cell. It avoids liquid-liquid junction potential. It maintains electrical neutrality without ~~direct~~ mixing of electrolytic solution.

* **Criteria of electrolytes used in salt Bridge:-**

① electrolytic solution should be inert towards electrode reaction i.e electrolyte of salt bridge should not take part in the reaction for eg:- KCl cannot be used in salt bridge if electrolytic solution contains Ag^+ ions.

② The transport number ~~for~~ (mobility of cation ~~and~~ or ions) should be same or nearly same.

S.Q — [Imp for eg:- KCl is preffered over other electrolyte because transport number of K^+ and Cl^- are same.]

The concentration of electrolyte should be high.

* **Construction of Galvanic cell (voltaic cell):-**

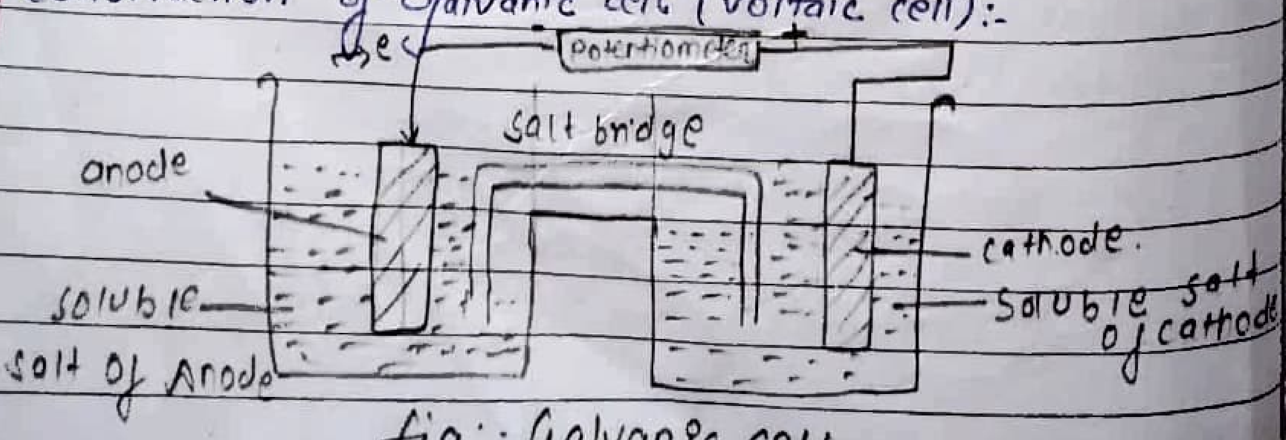


fig:- Galvanic cell.

PAGE NO.:
DATE: / /

For eg:-

$Zn \longrightarrow Zn^{++} + 2e^-$, $E^0ox = 0.77V$ $[E^0 Zn/Zn^{++} = 0.77V]$

$Zn^{++} + 2e^- \longrightarrow Zn$, $E^0red = -0.77V$ $[E^0 Zn^{++}/Zn = -0.77V]$.

* Types of electrode

Imp (1) primary reference electrode

Imp Standard Hydrogen electrode (SHE)

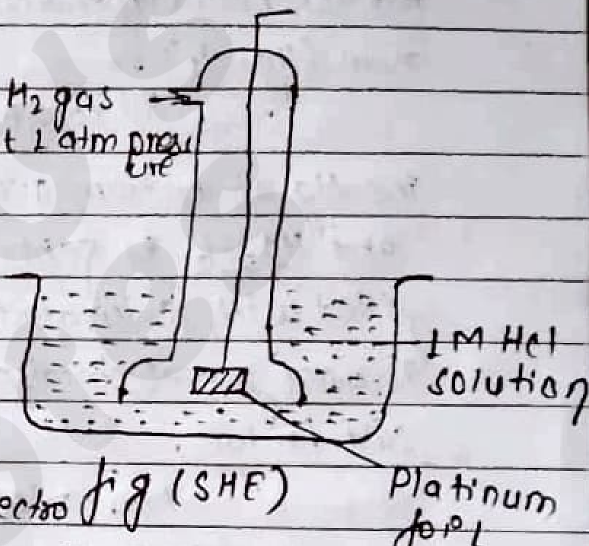


fig (SHE)

Hydrogen electrode is a gas electrode in which a platinum foil is emerged in 1 M HCl solution at 25°C, pure and dry H_2 gas is admitted through the narrow inlet maintaining 1 atm pressure. In this electrode, hydrogen gas is reverseble to H^+ of HCl. Depending upon nature of counter electrode, Hydrogen electrode act as both anode or cathode. Electrode potential of standard hydrogen electrode (SHE) is taken as zero (0).

If it act as anode then oxidation half reaction is

$\frac{1}{2} H_2 \longrightarrow H^+ + e^-$ [anode is always oxidation]

If it act as cathode, then Reduction half reaction is

$H^+ + e^- \longrightarrow \frac{1}{2} H_2$ [cathode is always Reduction].

+ = can store
− = cannot store.

(−) = Red . Potential
(+) = Oxidation potential

PAGE NO.:
DATE: / /

Here

① Emf = $E^{\circ}_{Sn^{4+}/Sn^{2+}} - E^{\circ}_{Fe^{3+}/Fe^{2+}}$

= 0.15 − 0.77
= −0.62 V.

Since emf is negative. Therefore this reaction is not feasible.

② gin Emf = $E^{\circ}_{Fe^{3+}/Fe^{2+}} - E^{\circ}_{Sn^{4+}/Sn^{2+}}$

= 0.77 − 0.15
= 0.62 V.

since emf is +ve . so the reaction is feasible or spontaneous.

-14th chaitra, 2078.

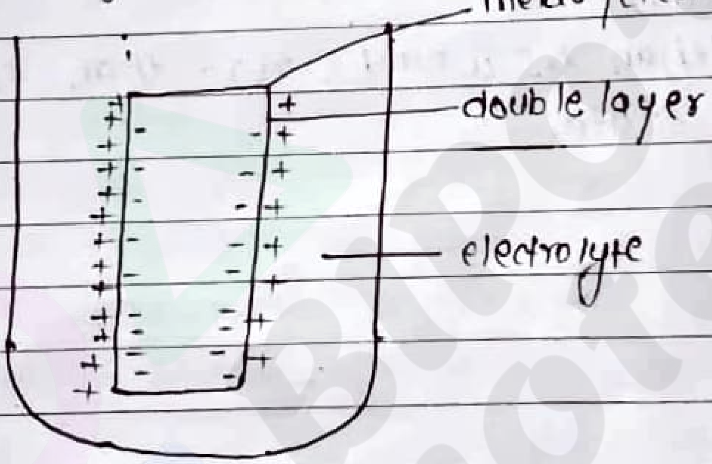
Gain - negative (Reduction)
loss - positive (oxidation)

PAGE NO.:
DATE: / /

Electrochemistry

* Electrode potential / Single electrode potential

↳ When a metal rod is diped into electrolytic solution of its soluble salt, either metal losses electron or accept electron. In this way the electron is either positive in charge or negatively charged. A charged electrode attracts oppositely charged ions in its vicinity (इकाई) and double layer of opposite charged is formed. The potential develop across the metal electrolyte due to formation of electrical double layer is called electrode potential or single electrode potential.



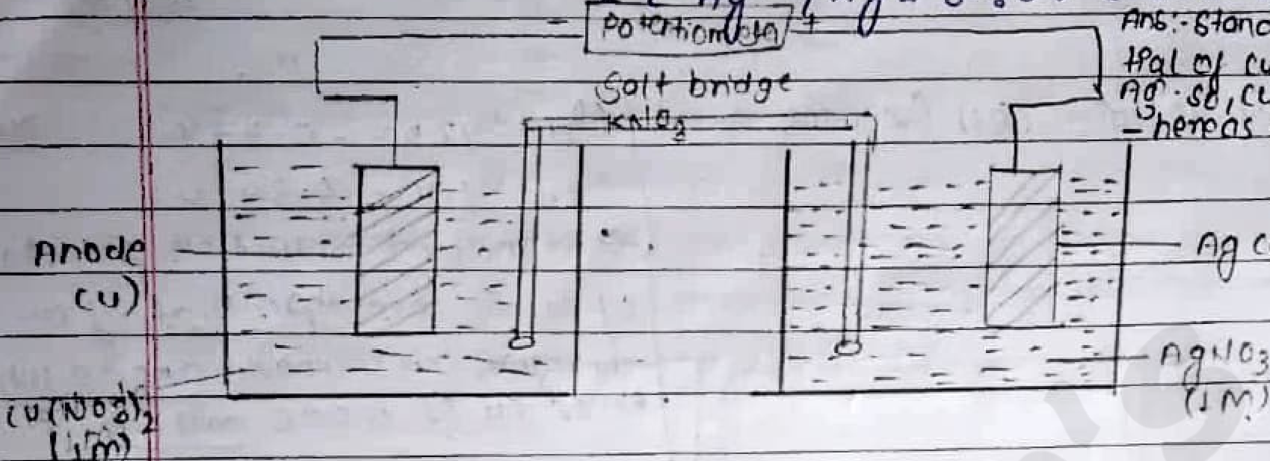
Electrode potential is defined as the potential developed due to formation of electrical double layer at the solid liquid interface when any metal dipped into its electrolytic solution. It is denoted by E.

Similarly, standard electrode potential is defined as electrode potential measure for an electrode at its 1 molal concentration of electrolytic solution at 25°c. It is denoted by E^{o}.

If electrode potential is measured in terms of loss of electrons by electrode (metal). It is called oxidation state E_{ox}. If electrode potential is measured in terms of gain of electrons by electrode then it is called reduction potential (E_{red})

DATE: / /

* Cu-Ag voltaic cell [$E^0_{Cu^{++}/Cu} = 0.34\,V$ (Anode)
$E^0_{Ag^{+}/Ag} = 0.80\,V$ (cathode)]



Ans:- Standard reduction potential of Cu is less than that of Ag. So, Cu is made anode whereas Ag is made cathode

→ cell notation:- Anode $Cu(s) / Cu(NO_3)_2 (1M) // AgNO_3 (1M) / Ag$ cathode.

→ cell reaction:-

① Anode half Reaction

$$Cu \longrightarrow Cu^{++} + 2e^-$$

② ~~cathoo~~ cathode half Reaction:

$$Ag^+ + e^- \longrightarrow Ag$$

③ Net cell Reaction:

$$Cu \longrightarrow Cu^{++} + 2e^-$$
$$\{Ag^+ + e^- \longrightarrow Ag\} \times 2$$
$$Cu + 2Ag^+ \longrightarrow Cu^{++} + 2Ag.$$

Oxidation potential:- $E^{-0}_{Li^+/Li}$

(+) to metal :- Reduction

metal to (+) :- oxidation.

PAGE NO.:
DATE: / /

* chlorine has highest Reduction potential.

* Electrochemical series:-

It is a series in which standard reduction potential of different elements are arranged in increasing order. elements at the top of series have list value for standard electrode potential indicating it is easy to oxidised the element. similarly, the element at the bottom of series have highest standard electrode potential and are easy to reduce

cathode half Reaction	notation	e° value.
$Li^+ + e^- \longrightarrow Li$	$E^0_{Li^+/Li}$	-3.04.
$K^+ + e^- \longrightarrow K$	$E^0_{K^+/K}$	-2.92.
⋮		
$2H^+ + 2e^- \rightarrow H_2$	$E^{-0}_{H^+/H_2}$	0.
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	$E^0_{Sn^{4+}/Sn^{2+}}$	0.15
$Cu^{2+} + e^- \rightarrow Cu^+$	$E^0_{Cu^{2+}/Cu^+}$	0.16.

Note ↳ Upper element displaced lower element but lower element cannot displace upper element

↳ The element above hydrogen have negative value of standard Reduction potential and the elements below the hydrogen has positive value of standard Reduction potential.

* Primary cell

A primary cell or battery is the one that cannot easily be recharged after once used. It is also called dry cell. The electrode reaction are irreversible in such cell.

It consist of zinc ~~cell~~ shell which serves as Anode whereas a graphite rod series as cathode. It is felied with mixture of ammonium chloride and zinc chloride. There is also mixture of carbon and MnO_2 outside graphite.

At anode: $Zn \longrightarrow Zn^{++} + 2e^-$

At cathode: $2NH_4^+ + 2e \longrightarrow 2NH_3 + H_2$.

* ~~Secondary cell~~.

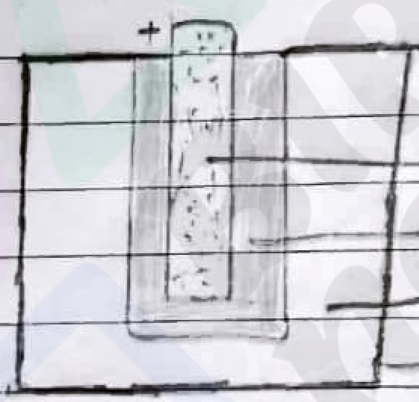


fig:- Dry cell (primary cell).

* Secondary cell:- Secondary cell is the type of cell which can be recharged after its complete discharge. Chemical energy is converted into electrical energy during discharge while electrical energy is converted into chemical energy during charging.

top = low
more value - Reducing
lower value - oxidizing

Mathi - Displace.
Tola - No displace.

PAGE NO.:
DATE: / /

Date:- 2078/12/19. (Sunday)

* Application of electrochemical series:-

(1) To predict whether a metal can or cannot liberate hydrogen gas from acid:-

Elements lying above hydrogen in electrochemical series can displace hydrogen gas from dilute mineral acid.

for eg:- $Zn + HCl_{(dil)} \longrightarrow ZnCl_2 + H_2$

$Cu + HCl_{(dil)} \longrightarrow$ no reaction

$Mg + H_2SO_{4(dil)} \longrightarrow MgSO_4 + H_2$.

(2) To compare the strength of oxidizing and reducing agent:-

Elements occupying top position in electrochemical series (having low reduction potential) are strong reducing agent whereas elements occupying bottom position (having higher reduction potential) are strong oxidizing agent.

(3) To predict whether a metal can or cannot displace other metals from their salt solution:-

Metals having lower reduction potential can displace those metals having higher reduction potential from their salt solution. It means metal lying above it electrochemical series can displace only those metals from their salt solution which lie below it electrochemical series.

for eg:- $Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$

But $Cu + ZnSO_4 \longrightarrow$ no reaction.

This is because $E^\circ_{Zn^{++}/Zn} = -0.77\,V$ where $E^\circ_{Cu^{++}/Cu} = 0.34\,V$

(100%) V.Imp.

Therefore the electrode potential of Cu electrode is 0.31 V.

Q Here, given electrode reaction:

a) $Zn \rightarrow Zn^{++} (1M) + 2e^-$, $E^o = +0.76 V$

b) $Sn^{++} (1M) + 2e \rightarrow Sn$, $E^o = -0.14 V$.

Here

Oxidation potential of Zn is given.

$\therefore E^o_{Zn^{++}/Zn} = -0.76 V$

$E^o_{Sn^{++}/Sn} = -0.14 V$.

since

$E^o_{Zn^{++}/Zn} < E^o_{Sn^{++}/Sn}$. So, Zn is made anode & Sn is made cathode.

$E^o = E^o_{cathode} - E^o_{anode}$.

$= -0.14 - (-0.76)$

$= 0.62 V$.

Cell notation:

$Zn / Zn^{++} (1M) // Sn^{++} (1M) / Sn$.