Electrochemistry

- Cell
  - Galvanic cell or voltaic cell
    - e.g. Daniel cell.
    - Chemical to electrical
    - spontaneous
    - $\Delta G^\circ < 0$
  - Electrolytic cell or voltameter - electrolysis
    - → electrical to chemical.
    - Non-spontaneous
    - → $\Delta G^\circ > 0$.
- Conductance

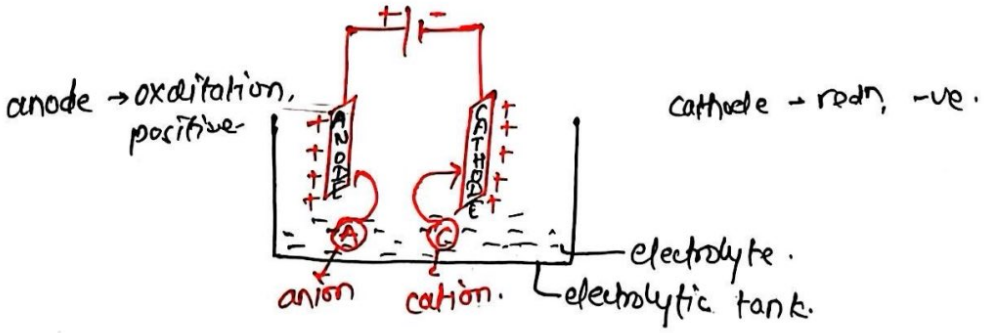
Anode :- always oxidation
Cathode :- " reduction

Electrolytic cell / Voltameter

→ electrical energy to chemical energy.
→ Electrolysis.
→ Cell in which process of electrolysis is carried out is known as electrolytic cell.

Electrolysis — electric current + breaking

↳ on passing electric current through the solution it dissociate into cation and anion. Cation deposited at cathode and anion at anode. This complete process is known as electrolysis.



Qualitative Analysis :-

Factors affecting cell rxn at electrode :-

1. Nature of electrolyte
2. State of electrolyte.
3. concentration of electrolyte [NACL]
4. charge density flown during electrolysis.
5. Nature of electrode. → inert → Pt
   → active → Cu, Ag. - - -

Abhishek

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① Electrolysis of fused electrolyte:-
molten

→ one type of cation and 1 type of anion.

→ $NaCl \longrightarrow Na^+ + Cl^-$
(Fused)

Cathode redn.

$Na^+ + 1e^- \longrightarrow Na$.

→ 1 Mole Na.

Anode oxdn.

$Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$

→ $2Cl^- \longrightarrow Cl_2 + 2e^-$

→ $\frac{1}{2}$ mole Cl_2.

Mole ration → $1 : \frac{1}{2} = 2:1$

wt. Ration :→ 46 : 71.

② Fused $MgCl_2$

$MgCl_2 \longrightarrow Mg^{++} + 2Cl^-$
Fused

Cathode

$Mg^{++} + 2e^- \longrightarrow Mg$.

Anode

$2Cl^- \longrightarrow Cl_2 + 2e^{\ominus}$

② aq. solution

aq. NaCl

Na^+, H^+ ✓ (Cl^-, OH^- ✓ ✓)

Br^- ✓, OH^-

NO_3^-, OH^- ✓

Au^+, H^+ ✓ (Mg^{+2}, H^+ ✓ ✓)

SO_4^{--}, OH^- ✓

ECS

Li, K, Ca, Na - ——— - H, Cu, Mg, Ag, Pt, A

Q. aq. NaCl.

Na^+, Cl^- ✓, H^+, OH^- → NaOH in solution.

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Cathode: $H^+ + e^- \longrightarrow \frac{1}{2}H_2$.

Anode: $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$

→ IF OH^- goes then;

$2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$

Q. On electrolysis of AgCl solution. Find the mole ratio of product of cathode: Anode?
(a) 1:2 (b) 2:1 (c) 1:1 (d) 2:3

→

AgCl solution

Ag^+ Cl^-

H^+ OH^-

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

Anode:- $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$

Mole ratio → C : A

$1 : \frac{1}{2} = 2:1$.

Q. On electrolysis of $CuSO_4$ solution. Find the mole ratio of product of anode : cathode?

Aq. $CuSO_4$

Cu^{++} SO_4^{--}

H^+ OH^-

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

Anode: $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$

$1 : \frac{1}{2}$

A : C → 1:2.

Q. Aq. solution of $MgCl_2$.

Mg^{++} Cl^-

H^+ OH^-

Cathode: $H^+ + e \longrightarrow \frac{1}{2}H_2$.

Anode: $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$.

A : C → $\frac{1}{2} : 1 = 1:2$.

C : A = 2:1

Q. On the electrolysis of $NaKSO_4$ solution. Find out the weight ratio of product at C:A?

(a) 1:4 (b) 1:2 (c) 1:8 (d) 1:1

aq. $NaKSO_4$

Na^+ SO_4^{--}

K^+ OH^-

H^+

Anode: $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$

cathode: $2H^+ + 2e^- \longrightarrow H_2$.

weight ratio →

C:A → 2:16

= 1:8.

Q. On the electrolysis of $AgNO_3$ solution. Find weight ratio of product at Anode: cathode?

(a) 1:27 (b) 27:1 (c) 2:27 (d) 27:2.

aq. $AgNO_3$

Ag^+ NO_3^-

H^+ OH^-

Cathode:- $2Ag^+ + 2e^- \longrightarrow 2Ag$.

Anode:- $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$

weight ratio → A:C → 16:216

= 2:27.

Q. On the electrolysis of aq. NaCl solution. The pH of resulting solution is:

(a) 7 (b) >7 (c) <7 (d) None.

aq. NaCl. - $Na^+ + Cl^-$ — ভাঙ্গে

$H^+ + OH^-$ — NaOH.

↳ more than 7.

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Q. On passing electric current through $CuSO_4$ solution. The pH of resulting solution is:-

(a) 7 (b) >7 (c) <7 (d) None.

eg. $CuSO_4 \longrightarrow Cu^{++} + SO_4^{--}$ → H_2SO_4 (acid)

$H^+ + OH^-$

Q. pH of aq. solution of NaCl is:-

(a) 7 (b) >7 (c) <7 (d) None

Special cases

① Electrolysis of very dilute solution

- In this solution, water is in excess. means H^+ and OH^- are in excess so, They deposit at cathode and anode.

eg. electrolysis of very dilute solution of NaCl:-

$NaCl \longrightarrow Na^+ + Cl^-$ (very dil)

$H_2O \longrightarrow H^+ + OH^-$ (excess)

Anode:- $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$

Cathode:- $2H^+ + 2e^- \longrightarrow H_2$.

C : A

1 : ½ = 2 : 1. - always in very dilute soln.

② Electrolysis in presence of Hg cathode

- In presence of Hg cathode, discharge potential of metal ion decreases. So, they will deposited at Hg cathode and they will form metal amalgum.

eg. electrolysis of aq. NaCl in presence of Hg cathode.

$NaCl \longrightarrow Na^+ + Cl^-$

$H_2O \longrightarrow H^+ + OH^-$

Cathode → Hg (amalgum)

Anode → $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$

Cathode → $Na^+ + e^- \longrightarrow Na \xrightarrow{Hg} Na\text{-}Hg$ (sodium amalgum)

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③ Electrolysis of dilute H_2SO_4

(A) On passing normal current

$H_2SO_4 \longrightarrow 2H^+ + SO_4^{--}$

$H_2O \longrightarrow H^+ + OH^-$

Anode:- $2OH^- \longrightarrow H_2O + \frac{1}{2}O_2 + 2e^-$

Cathode: $2H^+ + 2e^- \longrightarrow H_2$.

(B) On passing high electric current

$H_2SO_4 \longrightarrow H^+ + HSO_4^-$

$H_2O \longrightarrow H^+ + OH^-$

Anode:- $2HSO_4^- \longrightarrow H_2S_2O_8 + 2e^-$
Marshall's acid.

Cathode: $2H^+ + 2e^- \longrightarrow H_2$.

④ Electrolysis by using same metal electrode

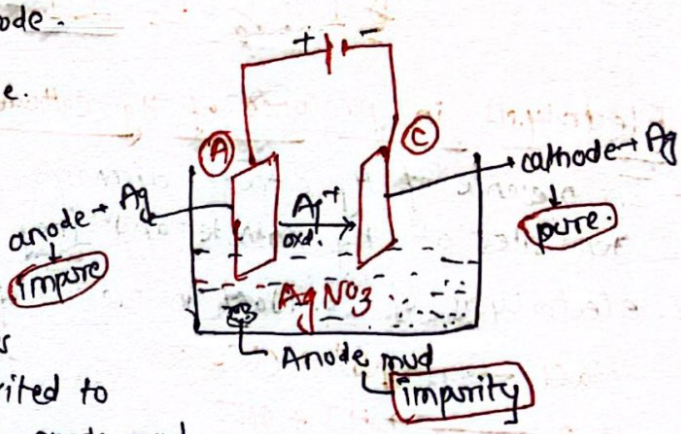
(A) Electrorefining

→ If in salt solution, same metal electrode are used then process is known as electrorefining.

eg. In $CuSO_4$ soln, Cu electrode

In $AgNO_3$ soln, Ag electrode.

In $AuCl_3$ soln, Au electrode.



→ On passing electric current, anode will oxidized and obtain Metal ion pass through the solution and finally deposited to cathode. while impurities obtained as anode mud.

→ wt. of impurities is negligible so,

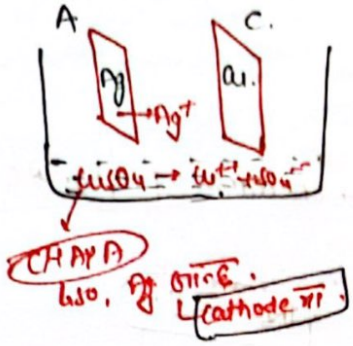
↓ in wt of anode = ↑ in wt of cathode

Anode:- $Ag(s) \longrightarrow Ag^+ + e^-$

Cathode:- $Ag^+ + e^- \longrightarrow Ag(s)$.

(B) Electroplating

→ Electrolysis of aq. $CuSO_4$ using Ag anode and Cu- cathode.



Anode rxn:

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

Cathode

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

Quantitative Analysis

(1) Faraday's 1st law:-

→ wt. of deposited ion ∝ amount of charge passed through the solution.

$W \propto Q$.

$W = ZQ$ Z → electrochemical equivalent

$I = \frac{Q}{t}$

$Q = It$

$W = ZIt$

$Z = \frac{W}{Q} = \frac{W}{It}$

$Z = \frac{E}{96500}$

→ When 1C charge is passed through the solution then wt. of deposited ion indicate Z.

→ When 1A current is passed for 1sec. then wt. of deposited ion indicate Z

$W = ZQ$

$Z = \frac{W}{Q} = \frac{gm}{C}$ unit → gm/C or gm/Axsec.

(2) Faraday's 2nd law:-

→ When two electrolytic cell are connected in series and same charge is passed. then wt. of deposited ion ∝ eq. wt

$W \propto E$

$\frac{W_1}{W_2} = \frac{E_1}{E_2}$ $\quad \frac{W_1}{E_1} = \frac{W_2}{E_2}$

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$$\frac{Z_1 \times \theta}{E_1} = \frac{Z_2 \times \theta}{E_2}$$

$$\frac{Z_1}{E_1} = \frac{Z_2}{E_2}$$

$E \propto Z$

$E = FZ$ $\quad F \rightarrow$ Faraday's constant $= 96500\ C$

$Z = \frac{E}{F} = \frac{E}{96500}$

1 mole e^- की charge $= 1F$

$\therefore \frac{W}{\theta} = \frac{E}{F}$

$E \rightarrow$ chemical eqv./eq. wt.

$\left(\frac{W}{E}\right) = \left(\frac{\theta}{F}\right) = \frac{I \times t}{F}$

$W = ZIt$

gm eq. — No of Faraday.

No. of gm eq = no. of Faraday = moles of e^-

Q. 965 A current is passed through the fused solution of Al_2O_3 for 1 hour. then find the weight of Al deposited?

(a) 370 (b) 350 (c) 300 ~~(d)~~ 324.

$\frac{W}{E} = \frac{I \times t}{F}$ $\quad$ E of Al = 9.

$W = \frac{965 \times 1 \times 60 \times 60 \times 9}{96500} = 9 \times 6 \times 6$

$= 324\ g$

Q. What current is to be passed for 0.25 sec for deposition of certain weight of metal which is equal to its Electro chemical equivalent?

~~(a)~~ 4A (b) 100 A (c) 200 A (d) 2A.

$W = Z$

$W = Z \times I \times t$

$1 = I \times t$

$I = \frac{1}{0.25} = 4A.$

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Q. Electrochemical equivalent of for Cu is 0.032 g/c. 0.5A current is passed through $CuSO_4$ solution for 50 min then find out the deposited of Cu.

(a) 4.9 (b) 5.2 (c) 4.5 (d) 4.0

$Z = 0.032$ g/c. $I = 0.5A$, $t = 50 \times 60 = 3000$ sec.

$W = ZIt$

$= 0.032 \times 0.5 \times 3000$

$= 4.9$.

Q. From $CuSO_4$ solution to deposit 0.01 gm equivalent Cu. How many columb charge is passed?

(a) 96500 (b) 0.95 (c) 965 (d) 96.5

$\left(\frac{W}{E}\right) = 0.01$. $Q = ?$

$\therefore$ no. of faraday $= 0.01$ f.

$\frac{Q}{F} = 0.01$

$Q = 0.01 \times F$.

$= 0.01 \times 96500$ C

$= 965$.

$\frac{W}{E} = \frac{Q}{F} = \frac{I \times t}{F}$

Q. Find out the charge in faraday on 1.4 gm ~~eq.~~ ion of N^{-3}?

mole.

(a) 4.2 (b) 4.5 (c) 5 (d) 4

gm-ion, gm-mol, gm-atom } 1 mole.

$Q = ?$

gm eq. = no. of faraday

mole $\times$ valency factor

$n \times V.f$ = no. of faraday.

1.4×3 = no. of faraday. $= Q$.

$\therefore$ $Q = 4.2$

For gases

$\left[\frac{W}{E}\right] = \frac{Q}{f} = \frac{Ixt}{F}$

$\frac{V}{Ve} = \frac{Q}{f} = \frac{Ixt}{F}$

V → volume of gas liberated

Ve → eq. volume of gas.

$= \frac{22.4}{\text{Valency factor}}$

H_2 gas →

$Ve = \frac{22.4}{2} = 11.2$ litre.

O_2 gas $(O \to 2, O_2 \to 4)$

$Ve = \frac{22.4}{4} = 5.6$ litre.

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Cl_2 gas

$V_e = \frac{22.4}{2} = 11.2$ litre

→ $\frac{W_1}{E_1} = \frac{W_2}{E_2}$ → mass - mass relation

→ $\frac{W}{E} = \frac{V}{V_e}$ → mass - volume relation

→ $\frac{V_1}{V_{e_1}} = \frac{V_2}{V_{e_2}}$ → volume - volume relation.

Q. 4.5g of aluminium (at mass = 27) is deposited at cathode from Al^{+3} soln by a certain quantity of electric charge. The volume of H_2 produced at STP from H^+ ion in solution by the same quantity of electric charge will be:-

(a) 44.8 l (b) 22.4 l (c) 11.2 l (d) 5.6 l

Sol

$\frac{W_{Al}}{E_{(Al)}} = \frac{V}{V_e}$ V_e of H_2 = 11.2

or $\frac{4.5}{9} = \frac{V}{11.2}$ ∴ V = 5.6 l.

Q. In the electrolysis of an aq. soln of NaOH, 2.8 l of oxygen gas at NTP was liberated at anode. How much of Hydrogen gas was liberated at cathode?

Sol

$\left(\frac{V_1}{V_{e_1}}\right)_{O_2} = \left(\frac{V_2}{(V_e)_2}\right)_{H_2}$

$\frac{2.8}{5.6} = \frac{V_2}{11.2}$ ∴ V_2 = 5.6 l.

Q. From 0.2 l, 0.1M $AgNO_3$ solution 0.1A current is passed ~~through~~ then to deposit half quantity of silver how much time is requ..

(a) 96500 (b) 9650 (c) 9600 (d) 96.50

gm eq = N × V

= 0.1 × 0.2

= 0.02.

half q. eq = $\frac{0.02}{2}$ = 0.01

$\because \frac{W}{E} = \frac{I \times t}{F}$

$0.01 = \frac{0.1 \times t}{96500}$

∴ t = 9650 sec.

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Q. From 200mL, 0.5M $CuSO_4$ solution to deposit 40% Cu, 0.2A current should be passed how many time?

(a) 38600s (b) 38000s (c) 96000s (d) 38500s.

$$gm\ eq = N \times V_L$$
$$= (0.5 \times 2)\ \frac{200}{1000} = 0.2.$$

$$40\%\ of\ 0.2\ deposited = \frac{40}{100} \times 0.2 = 8 \times 10^{-2}$$

$$\because\ 8 \times 10^{-2} = \frac{0.2 \times t}{96500}$$

$$t = \frac{8 \times 10^{-2} \times 96500}{0.2} = \frac{\overset{4}{\cancel{8}} \times 9650}{\cancel{2} \times 10^{-1}} = 9650 \times 4$$
$$= 38600$$

Q. To deposit 4gm Ca (at wt = 40) (eq. wt = 20) cost of electricity is Rs 5. then find out the cost of electricity to deposit 18gm Al (at wt = 27) (eq. wt = 9).

(a) 33 (b) 55 (c) 50 (d) 38

$$gm\ eq\ of\ Ca \rightarrow \frac{4}{20} = \frac{1}{5}$$

$$gm\ eq\ of\ Al = \frac{18}{9} = 2.$$

$$\because\ \frac{1}{5} \rightarrow 5$$

$$\therefore\ 2 \rightarrow 5 \times 5 \times 2$$
$$= 50\ Rs$$

Q. During electrolysis of aq. $AgNO_3$ (H^+ & Ag^+), 9.65A current is passed for 10 min. find:-

(i) wt of Ag (208 = 108) deposited at cathode. (NO_3^-, OH^-)

(ii) Volume of gas liberated at anode.

Sol

$$\frac{W}{E} = \frac{I \times t}{F}$$

$$\frac{W}{108} = \frac{9.65 \times 10 \times 60}{100\ 96500}$$

$$\therefore\ W = 1.08g \times 6 = 6.48g.$$

$$\frac{V}{V_e} = \frac{I \times t}{F}$$

$$\frac{V}{5.6} = \frac{9.65 \times 10 \times 60}{96500}$$

$$\therefore\ V = \frac{5.6 \times 60}{100} = 0.336L.$$

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Q. $AuCl_3$, $AgNO_3$ & $CuSO_4$ solution are connected in series from the 3F charge is passed then find out the mole ratio of metal ion deposited at cathode?

(a) 2:6:3 (b) 4:6:3 (c) 2:6:5 (d) 3:6:3

$AuCl_3$	$AgNO_3$	$CuSO_4$
3F	3F	3F
gm eq = 3	3	3
mole = 3/3 = 1	mole = 3/1 = 3	mole = 3/2

= 2:6:3

Q. From a solution electric current is passed for 193 sec than at NTP 2.24 Litre H_2 is obtained then find out the valve of current in ampere.

(a) 100 A (b) 10 A (c) 90A (d) 50A

$$\frac{V}{Ve} = \frac{W}{E} = \frac{Q}{F} = \frac{I \times t}{F} \quad \therefore \frac{V}{Ve} = \frac{I \times t}{f}$$

$$\therefore \frac{2.24}{11.2} = \frac{I \times 193}{96500}$$

Q. Silver voltameter and water voltameter are connected in series then in 1st cell 10.8gm Ag deposit then find out the deposit volume of O_2 at NTP?

(a) 0.56 lit (b) 5.6 lit (c) 5.4 lit (d) 0.54 lit

Q. On the electrolysis of water 4 mol electron From, anode to cathode the find out of volume of obtained gases at NTP?

(a) 22.4 lit (b) 2.24 lit (c) 20 lit (c) 54 lit (e) 67.2 litre

$$\frac{V_{O_2}}{Ve} = 4$$

4 O_2 = 5.6.

$V_{O_2} = 4 \times 5.6 = 22.4$.

$V_{H_2} = 4 \times 11.2 = 44.8$.

total volume = $V_{O_2} + V_{H_2}$

= 22.4 + 44.8

= 67.2 lit.

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Q) Find no. of faraday and no. of coulomb charge involve in following process.

(a) To reduce 0.2 mole MnO_4^- in acidic medium → A = 5 moles in Mn

(b) ↳ no. of faraday = gm eqv = no. of mole.

∴ 1 mole MnO_4^- = 5F

0.2 mole MnO_4^- = 5 × 0.2 = 1F

= 1 × 96500C

= 96500C.

(b) To reduce 0.2 mole MnO_4 in basic medium → 1 mole.

1 mole MnO_4^- = 1F

∴ 0.2 mole MnO_4 = 0.2 F

= 0.2 × 96500C.

Q. H_2O - electrolysis

Anode	Cathode
O_2	H_2
2.8 lit	H_2 = ?

$$\frac{V_{O_2}}{V_{eq}} = \frac{V_{H_2}}{V_{eq}}$$

$$\frac{2.8}{5.6} = \frac{V_{H_2}}{11.2}$$

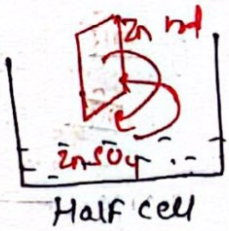
$\therefore V_{H_2}$ = 5.6 litre.

$M^+ + e^- \longrightarrow M$ → reduction.

$M \longrightarrow M^+ + e^-$ → oxidation.

Electrode:- metal dipped into its own solution → electrode.

e.g. Zn rod dipped into $ZnSO_4$ solution.



Electrode potential

Red. potential
Cathode
E_{RP}
E°_{RP} ↳ standard.

Oxd. potential
Anode
E_{OP}
E°_{OP} ↳ standard. ↳ T = 25°C, 1 Molar

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$\mathcal{E}^\circ_{m+2/m}$ ↳ standard redn potential $\boxed{SRP}$

$\mathcal{E}^\circ_{m/m+2}$ ↳ standard oxdn potential $\boxed{SOP}$

→ $Zn \rightarrow Zn^{+2} + 2e^{\ominus}$ $\quad \mathcal{E}^\circ_{op} = 0.71\,eV$

$\boxed{\begin{array}{l} \mathcal{E}^\circ_{op} - \text{fixed} \\ \mathcal{E}_{op} \rightarrow \text{variable} \end{array}}$

→ $Cu^{+2} + 2e^- \longrightarrow Cu$. $\quad \mathcal{E}^\circ_{RP} = \mathcal{E}^\circ_{Cu+2/Cu}$.

→ $Zn^{+2} + 2e^- \longrightarrow Zn$. $\quad \mathcal{E}^\circ_{RP} = -0.76\,V$

↳ $Zn \longrightarrow Zn^{+2} + 2e^-$ $\quad \mathcal{E}^\circ_{op} = +0.76\,V$

$$\boxed{\mathcal{E}^\circ_{RP}(m^{+n}/m) = -\mathcal{E}^\circ_{op}(m/m^{n+})}$$

→ $Cu^{+2} + 2e^- \longrightarrow Cu$: $\mathcal{E}^\circ_{RP} = 0.34\,V$] ×2
↳ fixed

$2Cu^{+2} + 4e^- \longrightarrow 2Cu$: $\mathcal{E}^\circ_{RP} = 0.34\,V$.

$\boxed{\mathcal{E}^\circ_{RP} \rightarrow SRP}$ $\quad \boxed{\mathcal{E}^\circ_{op} \rightarrow SOP}$

~~Galvanic cell~~

* No. of e⁻ transferred

(i) balance other than H & O.

(ii) O लाई H_2O ले (balance)

(iii) H लाई H^+ ले (balance)

(iv) charge → e^- (balance)

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O$

$IO_3^- + 6H^+ + 6e^- \longrightarrow I^- + 3H_2O$

↳ (No. of Faraday transferred)

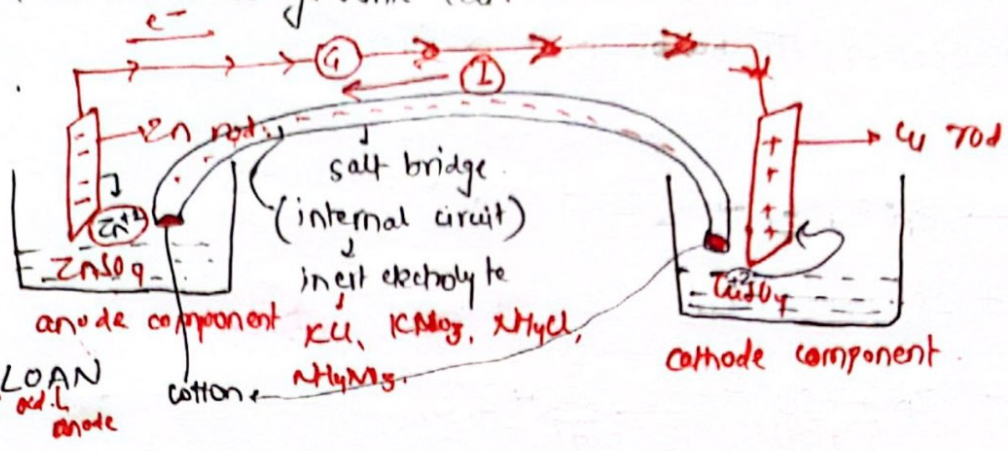
$Br_2 + 6H_2O \longrightarrow 2BrO_3^- + 12H^+ + 10e^-$

‡ Galvanic cell | Voltaic cell

e.g. Daniel cell.

→ A device which is used to convert chemical energy into electrical energy ~~into elect~~ is known as galvanic cell.

→



@ LOAN
left oxd. anode

$Zn \longrightarrow Zn^{+2}$

$Cu^{+2} \longrightarrow Cu$

$Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu$ (redn. / oxd.)

→ redox rxn.
→ spontaneous
→ ΔG = -ve.
→ emf = +ve.

→ In electrochemical series, upper metal act as anode & show oxidation while lower metal act as cathode and show redn.

→ If anode is Zn & cathode is Cu then that Galvanic cell is known as Daniel cell.

– In anode compartment Zn rod is dipped in $ZnSO_4$ and show oxidation due to which it is a -ve electrode and this half cell is known as oxidation half cell.

– In cathode compartment, Cu rod is dipped in $CuSO_4$ and show reduction due to which it is +ve electrode and this half cell is known as reduction half cell.

– When both electrodes are connected with a wire

ⓐ e^- will flow from anode to cathode.

ⓑ In external circuit, current will flow from cathode to anode.

ⓒ while in internal (salt bridge) circuit, current will flow from anode compartment to cathode compartment.

– weight of Zn rod ↓es while Cu rod ↑es.

→ conc. of $ZnSO_4$ sol^n ↑es while conc. of $CuSO_4$ solution ↓es.

→ Galvanic cell rxn is exothermic so. temp^r of both half cell ↑es.

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→ Galvanic cell मा redox reaction is spontaneous. i.e. $\Delta G = -ve$.

Cell Representation

$\boxed{\text{oxidation half cell} \,||\, \text{Red}^n \text{ half cell}}$

→ $\overset{\ominus}{Zn} | Zn^{+2}_{(aq)} \,||\, Cu^{+2}_{(aq)} | \overset{\oplus}{Cu}$.

→ In cell representation मा balancing is not required.

Cell rxn

(A) Oxd :- $Zn \longrightarrow Zn^{+2} + 2e^-$

(B) Red^n :- $Cu^{+2} + 2e^- \longrightarrow Cu$.

Net rxn → $Zn + Cu^{+2}_{(aq)} \longrightarrow Zn^{+2}_{(aq)} + Cu$.

Q. Aluminium rod was dipped in $\overset{+3}{Al_2}(SO_4)_3$ solution & Pb rod was dipped in $\overset{+2}{Pb}SO_4$ soln. Then find out :-

(a) cell representation

$\ominus\ Al | Al^{+3}_{(aq)} \,||\, Pb^{+2}_{(aq)} | Pb\ \oplus$

C_1 C_2.

(b) Cell rxn

Anode → $Al \longrightarrow Al^{+3} + 3e^-$ ×2

Cathode → $Pb^{+2} + 2e^- \longrightarrow Pb$ ×3

Net rxn → $2Al + 3Pb^{+2}_{(aq)} \longrightarrow 2Al^{+3}_{(aq)} + 3Pb$.

$\boxed{\begin{array}{l} -ve \text{ electrode} \rightarrow Al \\ +ve \text{ electrode} \rightarrow Pb. \end{array}}$

Q. Silver rod was dipped in AgCl solution and Cd rod was dipped in $CdCl_2$ solution. Then find out :-

ECS – माथि
anode.

(a) cell representation.

$_{(s)}Cd | Cd^{+2}_{(aq)} \,||\, Ag^{+1}_{(aq)} | Ag_{(s)}$

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(b) cell reaction.

Anode → $Cd \longrightarrow Cd^{+2}_{(aq)} + 2e^-$

Cathode → $[Ag^{+}_{(aq)} + e^- \longrightarrow Ag] \times 2$

Net rxn → $Cd_{(s)} + 2Ag^{+1}_{(aq)} \longrightarrow Cd^{+2}_{(aq)} + 2Ag_{(s)}$

(c)

-ve electrode → Cd.

+ve electrode → Ag.

# Electrolytic cell		Galvanic cell.	
Anode ⊕	Cathode ⊖	Anode ⊖	Cathode ⊕
oxidation	reduction	oxidation	reduction
out flow of e^-	in flow of e^-	out flow of e^-	in flow of e^-
in flow of I	out flow of I	in flow of I	out flow of I

Salt Bridge construction

① In the construction of salt bridge, we dissolve gelation or agar agar in hot & conc. inert solvent like KCl / NH_4NO_3 / NH_4Cl. (→ to make semi solid.)

② It maintain the ionic mobility of cation & anions same.

③ It maintains electrical neutrality in both vessels.

④

* Numerical section

Q. KCl is not used as an inert electrolyte in salt bridge for the cell.

$Cu|CuSO_4 \;||\; AgNO_3|Ag$. Why?

→ Cl react with Ag^+ & form AgCl ppt.

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Electrochemical series

Li → Cs, R
K → Ba, Sr
~~Na~~ Ca
Na
Mg
Al
Zn → Mn, H_2O
Cr
Fe
Cd → Co
Ni
Sn
Pb
H_2
Cu
Hg
Ag
Pt
Au.

SRP ↑ standard redn potential.

M_1: SRP = -3.0 (A)

M_2: SRP = -2.8 (C)

Q. $E^\circ_{A^{+1}/A} = -0.44$. (C)
(SRP)

$E^\circ_{B/B^{+2}} = +0.76V$
(SOP) SRP = -SOP
= -0.76V.

∴ SRP = -0.76V. (A)

जिसको SRP कम त्यो anode र जिसको बढी त्यो cathode.

Calculation of standard emf of cell

$$E^\circ_{cell} = (E^\circ_C)_{RP} - (E^\circ_A)_{RP}$$

$$E^\circ_{cell} = \text{SOP of anode} + \text{SRP of cathode}$$

$$= (E^\circ_A)_{OP} + (E^\circ_C)_{RP}.$$

Zn/Zn^{+2} → oxd.
Cu^{+2}/Cd → redn.

Q. $E^\circ_{Zn^{+2}/Zn} = -0.76V$ & $E^\circ_{Cu^{+2}/Cu} = 0.34V$. Find E° cell.
(Anode) (Cathode)

→

$$E^\circ_{cell} = (E^\circ_C)_{RP} - (E^\circ_A)_{RP}$$
$$= 0.34 - (-0.76)$$
$$= 1.10V.$$

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Q. Ni rod was dipped in $Ni(NO_3)_2$ solution and Al rod was dipped in $Al(NO_3)_2$ solution. Find :- $E^\circ_{Al^{+3}/Al} = -1.66V$ → Anode.

$E^\circ_{Ni^{+2}/Ni} = -0.25V$. → cathode.

(a) cell representation

(b) E°_{cell}

(c) cell rxn

→ (a) $\underset{(s)}{Al} | \underset{(aq)}{Al^{+3}} || \underset{(aq)}{Ni^{+2}} | \underset{(s)}{Ni}$ (e)

(b) $E^\circ_{cell} = (E^\circ_C)_{RP} - (E^\circ_A)_{RP}$

$= -0.25 - (-1.66)$

$= -0.25 + 1.66$

$= 1.51V$.

(c) cell rxn

cathode → $Ni^{+2} + 2e^- \rightarrow Ni] \times 3$

anode → $Al \longrightarrow Al^{+3} + 3e^-] \times 2$.

Net rxn

$3\underset{(aq)}{Ni^{+2}} + 2\underset{(s)}{Al} \longrightarrow 3\underset{(s)}{Ni} + 2\underset{(aq)}{Al^{+3}}$.

Q. $E^\circ_{mg/mg^{+2}} = +2.37V$. (A)
$\llcorner SOP$. $\llcorner SRP = -2.37V$.

$E^\circ_{Zn^{+2}/Zn} = -0.76V$. (E)

(a) cell representation.

~~Mg/Mg+2~~ $\underset{(s)}{Zn} | \underset{(aq)}{Zn^{+2}} || \underset{(aq)}{Mg^{+2}} | \underset{(s)}{Mg}$.

(b) E°_{cell}.

$E^\circ_{cell} = (E^\circ_C)_{RP} - (E^\circ_A)_{RP}$

$= -0.76 - (-2.37)$

$= 1.61V$.

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(c) cell rxn

Cathode → $Zn^{+2}_{(aq)} + 2e^- \longrightarrow Zn_{(s)}$

anode → $Mg_{(s)} \longrightarrow Mg^{+2}_{(aq)} + 2e^-$

Net rxn → $Zn^{+2}_{(aq)} + Mg_{(s)} \longrightarrow Zn_{(s)} + Mg^{+2}_{(aq)}$

Q. Ni rod was dipped in $Ni(NO_3)_2$ solution and Ag rod was dipped in $AgNO_3$ solution. Then find out :-

$E^\circ_{Ni^{+2}/Ni} = -0.25V$ (A)

$E^\circ_{Ag^{+}/Ag} = 0.80V$ (C)

(a) cell representation

(b) cell rxn

(c) E°cell

(a) → $Ni_{(s)} | Ni^{+2}_{(aq)} || Ag^{+}_{(aq)} | Ag_{(s)}$

(b) cell rxn

Cathode → $Ag^{+}_{(aq)} + 1e^- \longrightarrow Ag_{(s)}$ × 2

anode → $Ni \longrightarrow Ni^{+2} + 2e^-$

$2Ag^{+}_{(aq)} + Ni_{(s)} \longrightarrow 2Ag_{(s)} + Ni^{+2}_{(aq)}$

(c) $E^\circ_{cell} = (E^\circ_C)_{RP} - (E^\circ_A)_{RP}$

$= 1.80 - (-0.25)$

$= 1.05V$.

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→ SRP increases down the series. (ECS)
→ SOP decreases down the series.
SRP of $H_2 = 0$.
→ Reactivity of metal decreases down the series.
→ Reactivity of non-metal ↑ increases down the series.
→ lowest SRP is of Li.
→ Highest SRP is of Fluorine.
→ strongest reducing agent in aq. medium → Li.
→ strongest reducing agent in gaseous medium → Cs.
→ Upper metal can displace salt solution of lower metal.
→

$$Fe + ZnSO_4 \longrightarrow FeSO_4 + Zn \quad (X)$$

(lower than Zn in ECS.)

$$ZnS + FeSO_4 \longrightarrow ZnSO_4 + Fe \quad (\checkmark)$$

→ for strongest reducing agent SRP को value less हुन पर्यो।
→ for strongest oxidising agent SRP को value more हुन पर्यो।

Stability of metal oxide

$$\overset{+2}{M}O \xrightarrow{\Delta} \overset{0}{M} + \frac{1}{2}O_2$$

(M: redn.)

metal को उसको SRP को value बढी हुँदै त्यो metal oxide unstable.

Cu
Hg
Ag — metal oxide (unstable).
Pt
Au

Production of H_2 gas

- with cold water → Li to Na (Most rxtive).
- with hot water → Mg to Cr.
- with steam → Fe to Pb. (less reactive).

* with dilute mineral acid → All metal above H_2 in ECS
eg. dil HCl, dil H_2SO_4

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$E^\circ_{Cr^{+3}/Cr} = -0.74\ V$

$E^\circ_{H^+/H_2} = 0\ V$

$E^\circ_{Fe^{+3}/Fe^{+2}} = 0.77\ V$

Strongest reducing agent = ?
→ Zn due to lowest SRP.

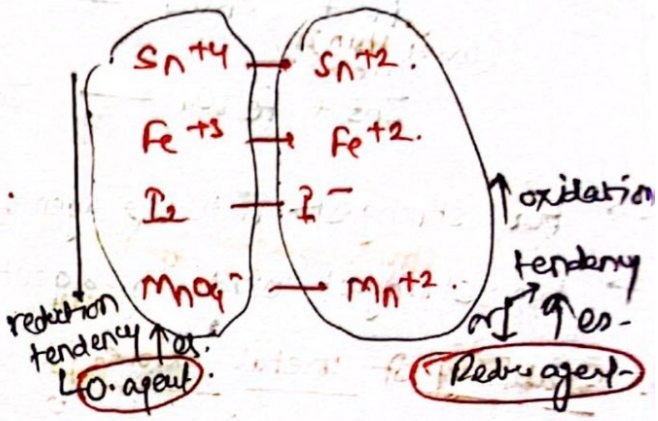
Highest oxidation tendency → Zn. ↳ reduces other itself oxidises.

Q. $E^\circ_{RP}(I_2/I^-) = 0.54$ → 3rd

$E^\circ_{RP}(MnO_4^-/Mn^{+2}) = 1.52$ → 4th.

$E^\circ_{RP}(Sn^{+4}/Sn^{+2}) : 0.1$ → Top of ECS.

$E^\circ_{RP}(Fe^{+3}/Fe^{+2}) = 0.1$ → 2nd.



strongest oxidant = ?
↳ O.A.

(a) Sn^{+2} (b) Sn^{+4} (c) ~~MnO_4^-~~ (d) Mn^{+2}

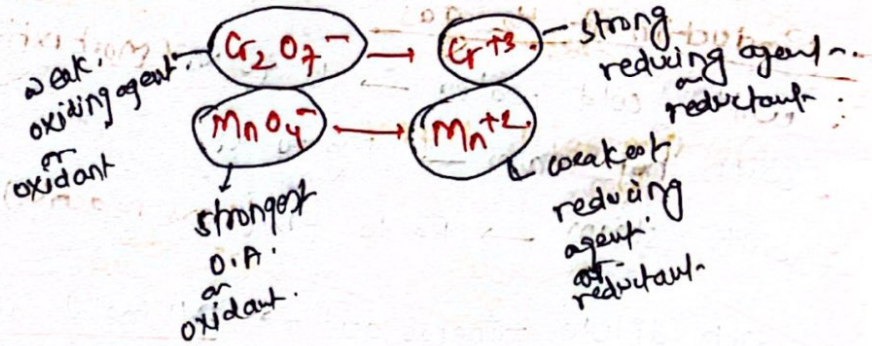
(a) ↓ strongest reductant ~ reducing agent.

(b) ↓ weakest oxidant.

(d) ↳ weakest reducing agent.

Q. $MnO_4^- \longrightarrow Mn^{+2}$ $E^\circ_{RP} = 1.51\ V$ → below.

$Cr_2O_7^{2-} \longrightarrow Cr^{+3}$ $E^\circ_{RP} = 1.4\ V$ → top



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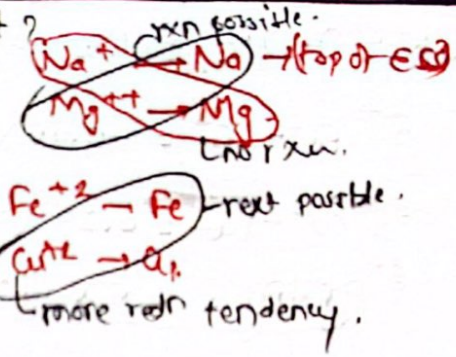
8. Which of the following statement is correct?

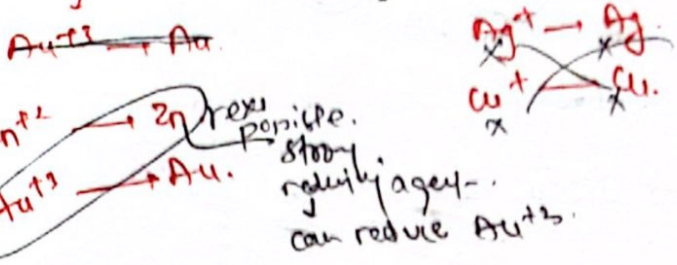
(a) Na^+ reduce by Mg.

(b) Fe^{+2} has more reduction tendency than Cu^{+2}

(c) Ag act as oxidising agent for Cu. (never)

(d) Au^{+3} can reduce by Zn.





Q. Zn^{+2} → Zn
Cu^{+2} → Cu
strong oxidising agent. can oxidise Zn.

(a) Zn^{+2} oxidise Cu^{+2}. False.

(b) Zn act as R.A for Cu. False

(c) Zn^{+2} oxidize Cu. False

(d) Cu^{+2} oxidise Zn. True.

Q. Which of the following give product.

(a) Mg (below) + $NaSO_4$ (top) → No product. (can't displace)

(b) Zn (top) + $FeSO_4$ (below) → $ZnSO_4$ + Fe.

Q. When Cu (below) spoon is dipped in $FeSO_4$ (top of ECS than Cu) solution. what will happen.

→ Nothing will happen.

Q. On the basic of following E° value strongest oxidizing agent/reduction tendency.

(a) $[Fe(CN)_6]^{3-}$ (weak oxid. agent) → $[Fe(CN)_6]^{4-}$ (strong reducing agent) $E^\circ_{RP} = 0.35$ (RP)

Fe^{+2} → Fe^{+3}, $E^\circ_{OP} = -0.77$ (SOP) → Fe^{+3} (strongest Fe^{+2}) → Fe^{+2} (weak reducing agent.) $E^\circ_{RP} = 0.77$ (SRP)

(a) Fe^{+3} (b) $[Fe(CN)_6]^{3-}$ (c) $[Fe(CN)_6]^{4-}$ (d) Fe^{+2}

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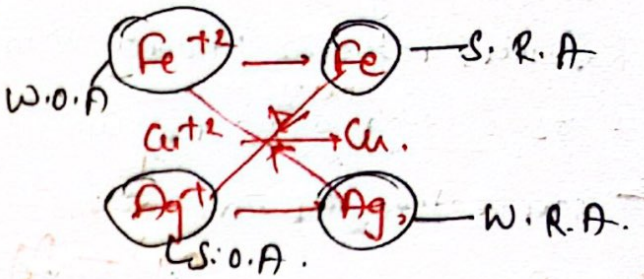
Q. Which of the following is correct.

- $E^\circ_{Fe^{+2}/Fe} = -0.44\,V$ (top)
  $E^\circ_{Cu^{+2}/Cu} = 0.34\,V$
  $E^\circ_{Ag^{+}/Ag} = 0.8\,V$ (below).



(a) Cu can displace iron from $FeSO_4$.

(b) Iron can displace Cu from $CuSO_4$.

(c) Silver can displace Cu from $CuSO_4$.

(d) Iron can displace Ag from $AgNO_3$.

Q. $E^\circ_{A^+/A} \rightarrow -0.34\,V$ (SRP)

$E^\circ_{B^+/B} \rightarrow -0.73\,V$ (SRP)

$E^\circ_{C/C^+} \rightarrow -0.32\,V$ (SOP)

SRP = 0.32 V

$B^+ \rightarrow B$ S.R.A.
W.O.A.

$A^+ \rightarrow A$

$C^+ \rightarrow C$ W.R.A
S.O.A.