

PHYSICAL CHEMISTRY
ELECTROCHEMISTRY

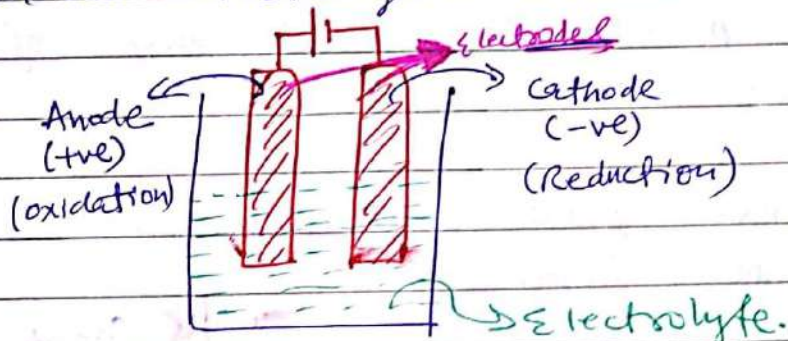
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☆☆ Electrolysis -

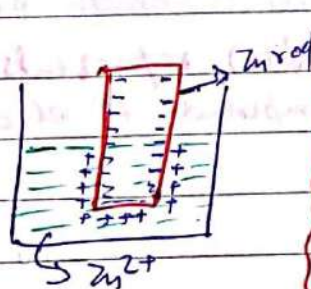
Electrical Energy \rightarrow Chemical Energy.

Here, a non-spontaneous redox rxn takes place in electrolysis with the help of electrical energy. (battery).

The apparatus in which electrolysis is carried out is known as electrolytic cell.



Electrode may be inert or reactive.



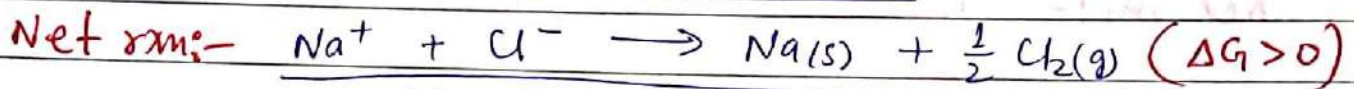
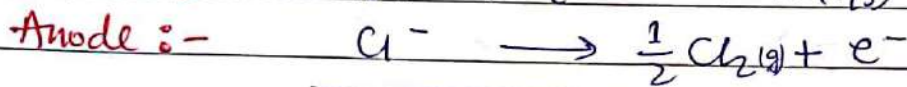
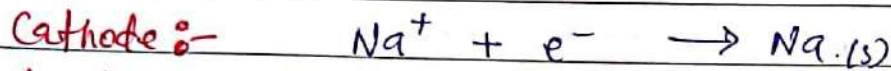
When a metal rod is dipped into its solution then polarity is developed and due to this potential is developed and it is measured at standard condition therefore it is known as standard electrode potential.

Standard Electrode potential is an intensive property.

True Electrolyte - Conducts electricity in molten (fused) form as well as aqueous form.

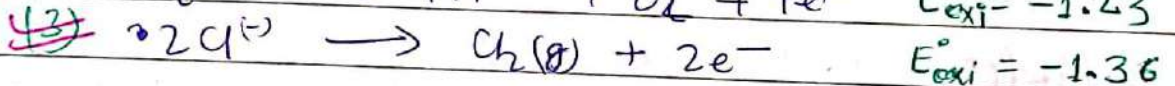
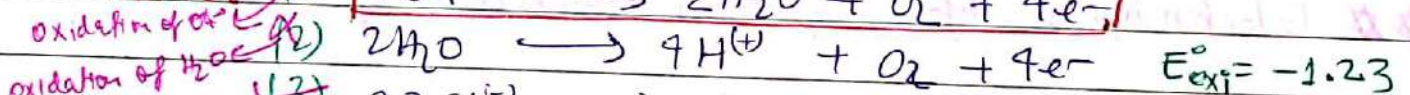
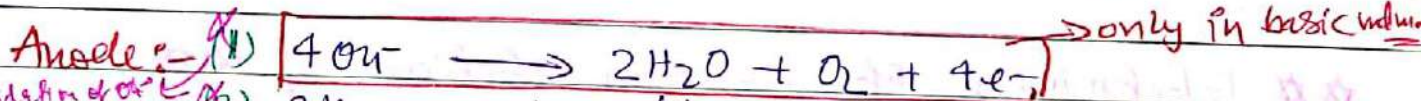
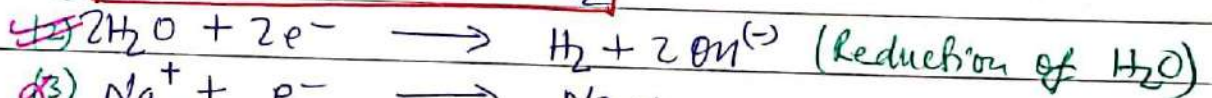
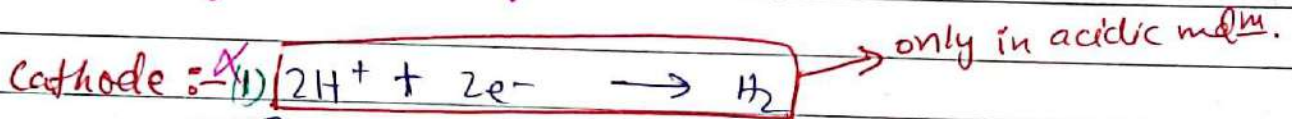
Non potential Electrolyte - Conducts electricity only in aq. form.

*** Electrolysis of molten (Fused) NaCl -



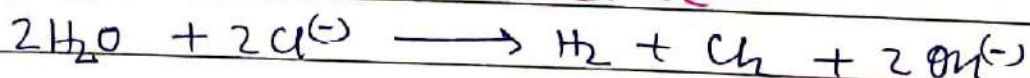
Note - Net cell rxn me kabhi bhi e^- ke darshan nahi honge.

*** Electrolysis of aqueous NaCl -



Note - Since it is experimentally found that O_2 is evolved at $E_{\text{oxi}}^\circ = -1.73 \text{ V}$ so before that Cl^- gets oxidized. The extra voltage of 0.50 V is called overvoltage. This will be the case with every halogen.

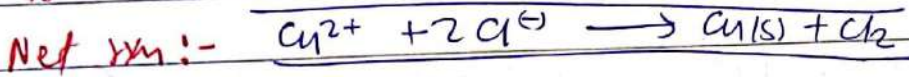
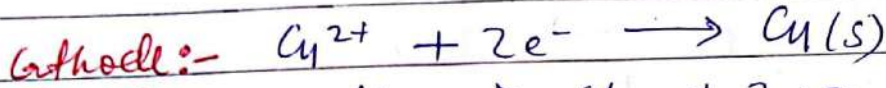
Hence, Net cell rxn would be -



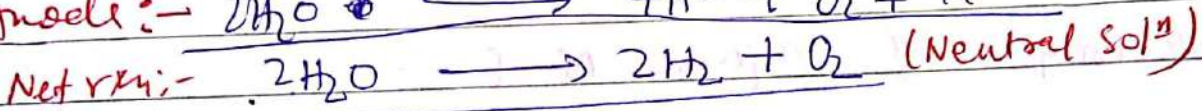
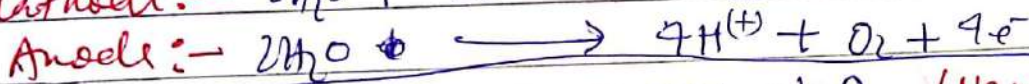
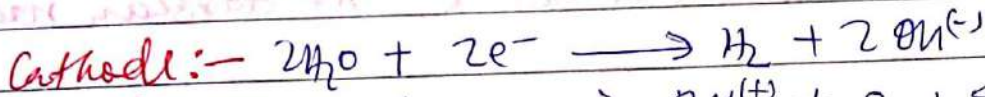
Na^+ will combine with OH^- to form NaOH .

Hence, the final solution would be basic in nature.

Electrolysis of aqueous solution of CuCl_2 -

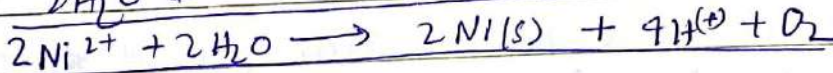
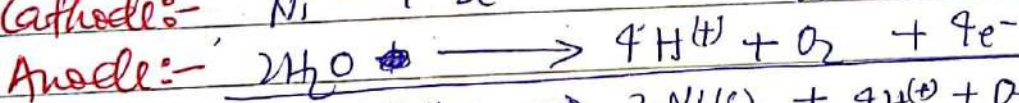
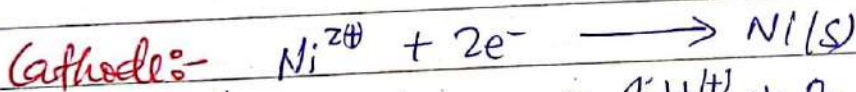


Electrolysis of aqueous Na_2SO_4 -



Note:- If any anion has max. oxidation state wrt unknown atom then oxidation of water takes place in place of that anion.

Electrolysis of aqueous solution of $\text{Ni}(\text{NO}_3)_2$ -



(Q) Which of the following metals produces H_2 gas with H_2O .

- (a) Mg (b) Mn (c) Cu (d) Ni.

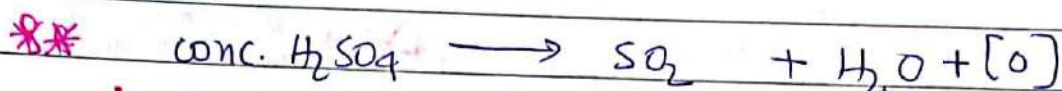
Ans \rightarrow (a) (b)

(Q) Which of the following metal produces H_2 gas with dilute H_2SO_4 .

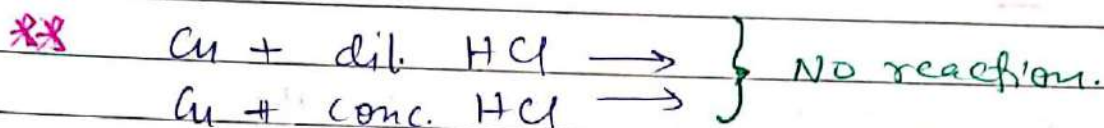
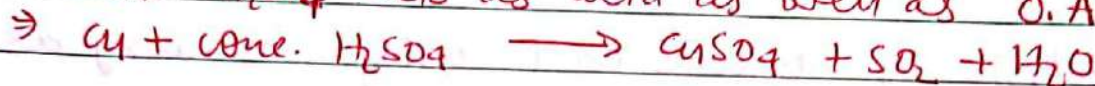
- (a) Mg (b) Cu (c) Mn (d) Na

Ans \rightarrow (a) (c) (d)

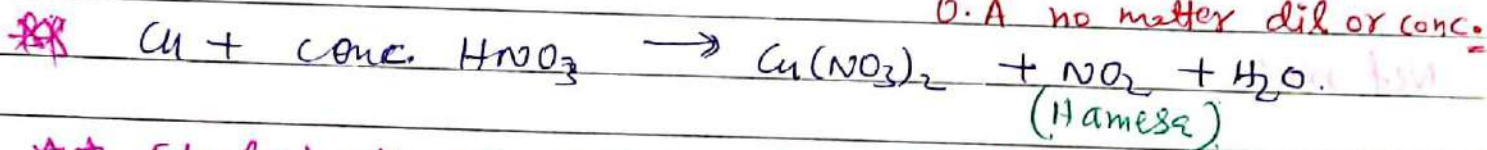
Note - Metals having reduction potential lesser than H^+ will produce H_2 with dilute acids.



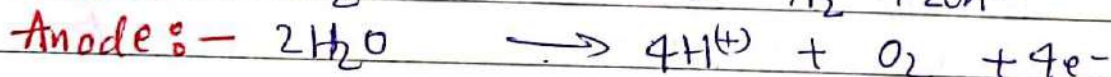
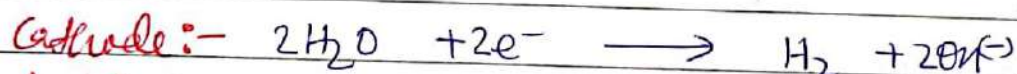
$\Rightarrow conc. H_2SO_4$ acts as acid as well as O.A $\Rightarrow SO_2$ ka banana sure hai.



Reason - Cl^- is in min oxidation state so it cannot be reduced further $\Rightarrow HCl$ can't act as an O.A no matter dil or conc.

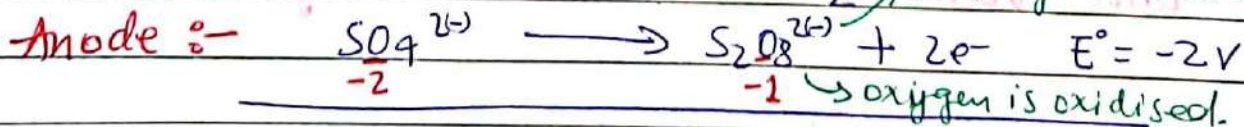
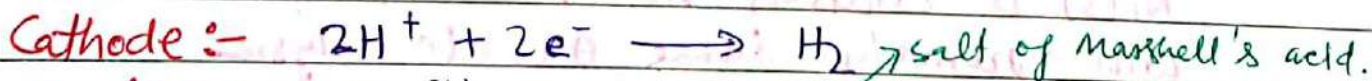


****** Electrolysis of very-very dilute NaCl -
 (\Rightarrow 4नी 4नी $\frac{1}{2}$) (Hint)



Net rxn :-

****** Electrolysis of very-very conc. H_2SO_4 -



Net rxn :-

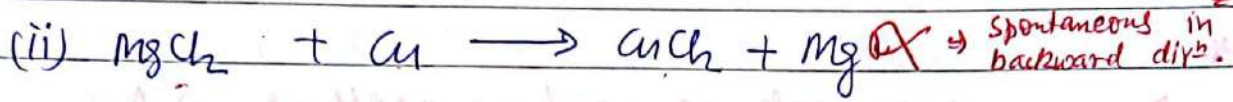
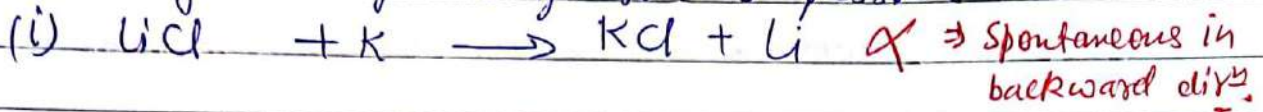
Note :- In case of dilute $H_2SO_4 \rightarrow H^+ \rightarrow$ reduction,
 $H_2O \rightarrow$ oxidation.

Note - (1) DECS is valid only when electrodes are not reactive,

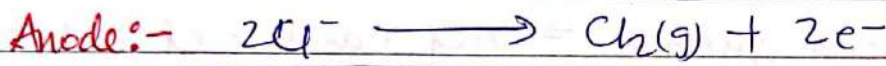
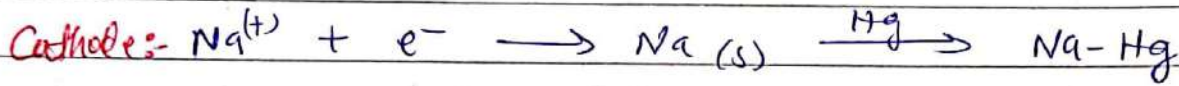
(2) All metals except Iron and Mercury form amalgam with

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(Q) Which of the following rxn is possible -

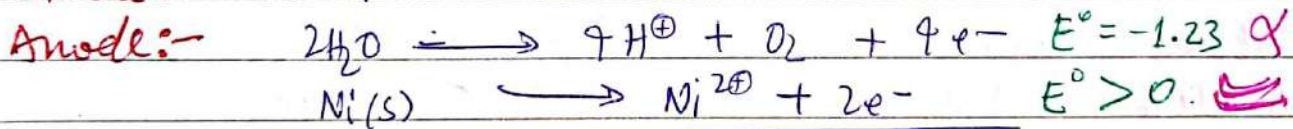
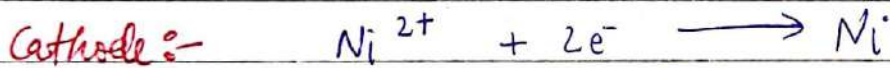


Electrolysis of aqueous NaCl using mercury as cathode - (Anode can be any) -



Net rxn:-

Electrolysis of aqueous $\text{Ni}(\text{NO}_3)_2$ using Ni as electrode -



Net rxn:-

Note: (1) Since in above case Ni^{2+} is reduced and Ni(s) is oxidised so molarity of $\text{Ni}(\text{NO}_3)_2$ solⁿ will remain same on electrolysis.

This is bcoz jitna Ni oxidise hua utna is Ni^{2+} reduce ho gaya.

(2) An (gold) ko chhor kar ~~active~~ ^{Koi} metal ki electrode le to metal hi oxidise hogi w.r.t H_2O .

(in case of active electrode).

Note - Kabhi bhi wahi rxn pelki jayegi jinka oxidation or reduction ki rxn same hogi.

ex H_2O ke rxn ko belet nahi sakte.

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** Faraday's law of Electrolysis -

1st law - $W \propto Q \Rightarrow W = ZQ \Rightarrow \boxed{W = ZIt}$

Z: Electrochemical Equivalence.

2nd law - $W \propto E \Rightarrow \frac{W}{E} = \text{constant} \Rightarrow \text{Gram-Equivalents} = \text{const.}$

$$\Rightarrow \frac{W_1}{E_1} = \frac{W_2}{E_2} = \dots = \frac{W_n}{E_n}$$

** Charge on 1 mole $e^- = 1 \text{ Faraday} = 96500 \text{ C.}$

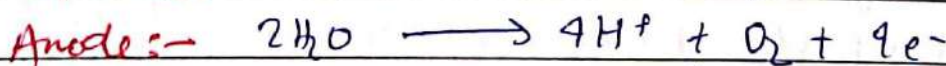
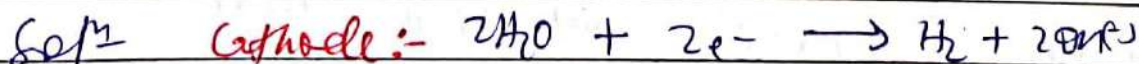
** No. of Faraday of current passed =
No. of gram-equivalent deposited or liberated.

$$\Rightarrow \text{No. of Faraday} = \text{No. of gram equi.} = \frac{Q}{96500} = \frac{It}{96500}$$

** If current efficiency is $x\%$ then -

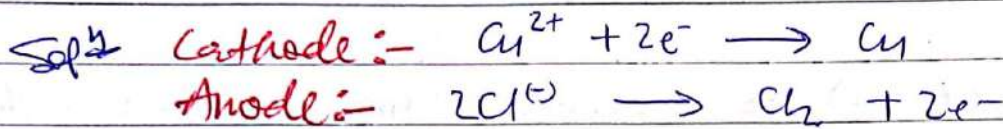
$$\text{No. of Faraday} = \text{No. of gram equi} = \frac{i \times \frac{x}{100} \times t}{96500}$$

(Q) 1.2 A current is passed for 9.65 min in aq. solⁿ of NH_4SO_4 . If the vol^m of gas evolved at cathode is 5.6 lt at S.T.P. Find mol. wt and volume of gas evolved at anode.



$$\Rightarrow x_{H_2} = x_{O_2} \Rightarrow \frac{5.6 \times 2}{22.4} = \frac{V}{22.4} \times 4 \Rightarrow V = 2.8 \text{ lt.}$$

(Q) If 5 A current is passed for 9.65 min in aq. solⁿ of CuCl₂ then find the vol^m of gas evolved at electrodes at STP.
Given current efficiency = 60%.

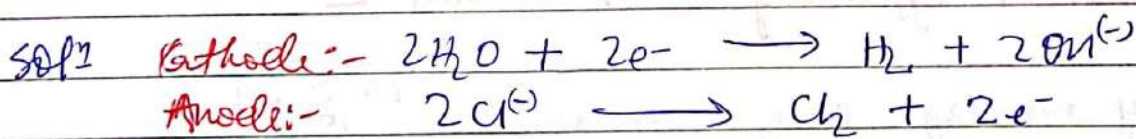


$$\text{No. of Faraday} = \frac{5 \times 9.65 \times 60 \times 60}{100 \times \frac{6500}{100} \times 100} = \frac{60 \times 300}{10^6} = \frac{18}{10^3} \text{ F}$$

$$= 1.8 \times 10^{-2} \text{ F}$$

$$\therefore \text{Vol}^m \text{ of } \text{Cl}_2 = \frac{1.8 \times 10^{-2} \times 22.4}{2} =$$

(Q) 1.2 A current is passed for 9.65 min in 1.11 gm CuCl₂ dissolved in water. Find the volume of gas evolved at electrodes at STP. Given, vol^m of solⁿ = 2 Lt.



$$\text{No. of Faraday} = \frac{1.2 \times 9.65 \times 60}{\frac{6500}{100} \times 100 \times 10} = \frac{72 \times 10^{-4}}{7.2 \times 10^3}$$

$$\% \text{ CuCl}_2 = \frac{1.21}{100} \times 2 = 0.02$$

$$\text{Gram equi. of } \text{H}_2 = 7.2 \times 10^{-3} \Rightarrow \text{moles of } \text{H}_2 = \frac{7.2 \times 10^{-3}}{2}$$

$$\text{Gram equi. of } \text{Cl}_2 = 7.2 \times 10^{-3} \Rightarrow \text{moles of } \text{Cl}_2 = \frac{7.2 \times 10^{-3}}{2}$$

Given equl. of $\text{OH}^- = 7.2 \times 10^{-3}$

$$\Rightarrow [\text{OH}^-] = \frac{7.2 \times 10^{-3}}{2} = 3.6 \times 10^{-3}$$

$$\begin{aligned} \therefore \text{pOH} &= -\log [\text{OH}^-] = -\log(3.6 \times 10^{-3}) \\ &= -(\log 3.6 + \log 10^{-3}) \\ &= -\log 3.6 + 3 \Rightarrow 3 - \log 3.6 \end{aligned}$$

$$\Rightarrow \text{pH} = 14 - \text{pOH} = 11 + \log 3.6$$

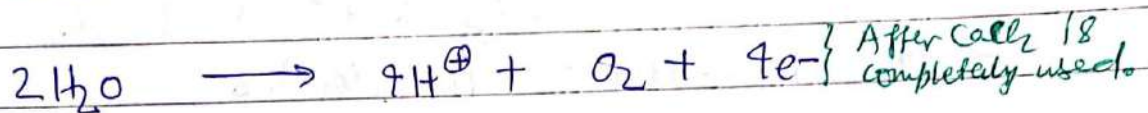
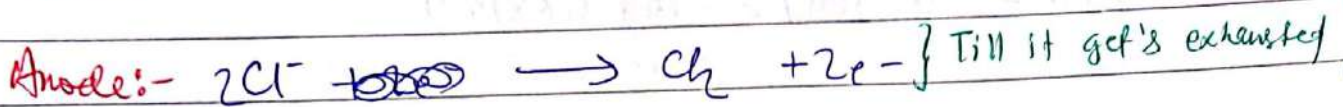
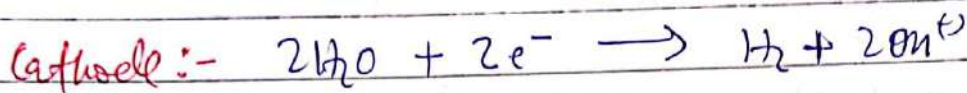
Note:- In above question, No. of Faraday of current passed is less than the ^{no. of} gram-equivalents of CaCl_2 so before all the CaCl_2 is used, ~~battery~~ current gets used up completely so the products at electrodes will be usual. i.e. H_2 at cathode and Cl_2 at anode.

However, if no. of faraday of current passed is more than the no. of gram-equivalents of CaCl_2 then, all the CaCl_2 will be used up before current passed is completely used up. In that case, after CaCl_2 gets exhausted, oxidation of water at anode starts to occur. And hence, we get unexpected products at electrodes. i.e. H_2 at cathode and Cl_2 and O_2 at anode.

(Q) If in previous question 1.2 A current is passed for 9.65 hrs they find the volume of gas evolved at ~~anode~~ electrodes, pH of the solⁿ and the time in which oxidation of Cl^- is stopped.

$$\text{Sol}^n \text{ No. of faraday} = \frac{1.2 \times 9.65 \times 60 \times 60}{96500 \times 100 \times 10} = \frac{12 \times 36}{10^3} = \frac{432}{10^3} = 0.432 \text{ F}$$

Now, we have $x_{CaCl_2} = 0.02$.



\therefore Remaining quantity of electricity after $CaCl_2$ is completely used = $(0.432 - 0.02) = 0.412 F$

$\therefore H_2, O_2, Cl_2$ gases are evolved.

Gram equi. of $Cl_2 = 0.02$

Gram equi. of $H_2 = 0.432$

Gram equi. of $O_2 = 0.412$

Moles of Gas = $\left(\frac{0.02}{2} + \frac{0.432}{2} + \frac{0.412}{4} \right)$

\therefore Vol^m of Gas = $(\text{Moles of Gas} \times 22.4) \text{ Lt.} = 24$

Now, To find pH -

Contribution of H^{\oplus} and OH^{\ominus} after $CaCl_2$ is completely used will neutralize each other making the solution neutral.

Hence, the pH of the solution will be contributed by the OH^{\ominus} generated initially.

$\therefore x_{OH^{\ominus}} = 0.02 \Rightarrow n_{OH^{\ominus}} = 0.02 \Rightarrow [OH^{\ominus}] = \frac{0.02}{2} = 0.01$

$\therefore pOH = -\log [OH^{\ominus}] = -\log 0.01 = 2$

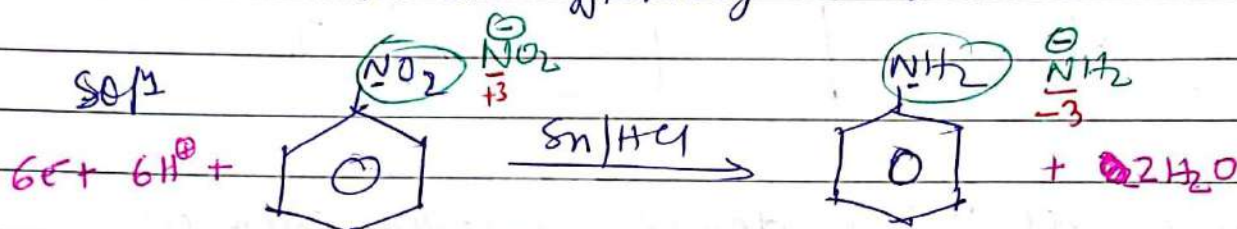
$\Rightarrow pH = 12$

Time in which oxidation of C^{2+} has stopped = t .

$$\therefore 0.02 = \frac{1.2 \times t}{96500} \Rightarrow t = 26.8 \text{ min.}$$

(Q) How much charge should be passed in 12.3 gm nitrobenzene to convert it into Aniline.

Given current efficiency = 50%.



$$\eta_{\text{ph-NO}_2} = \frac{12.3}{12.3 \times 10} = \frac{1}{10} = 0.1 \quad \eta_{\text{factor}} = 6$$

$$\kappa_{\text{ph-NO}_2} = 0.1 \times 6 = 0.6$$

$$\therefore \text{No. of faraday} = 0.6 \Rightarrow 0.6 = \frac{Q}{96500} \Rightarrow Q = 0.6 \times 96500$$

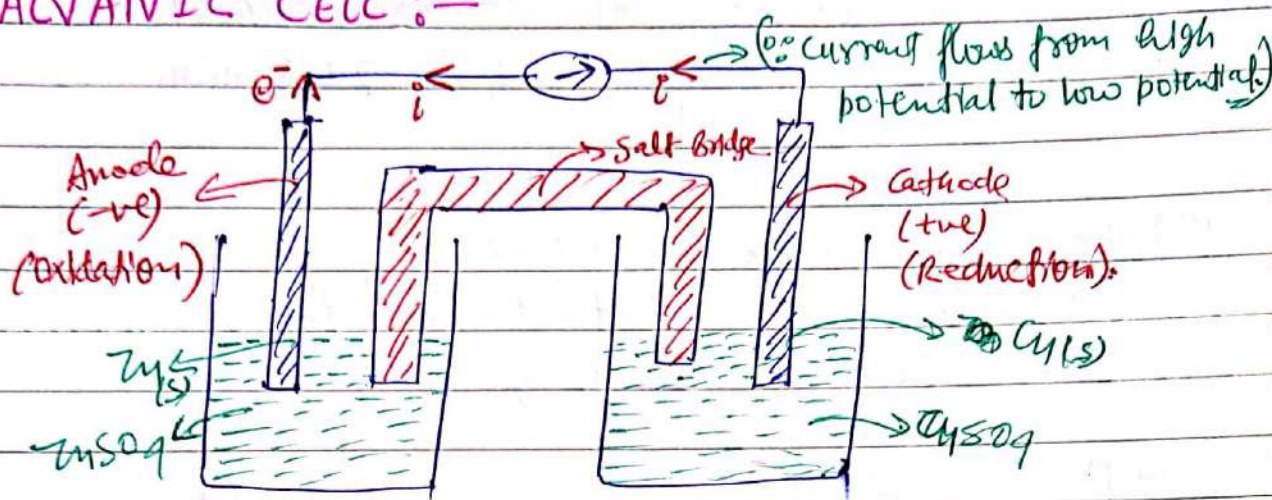
But since current efficiency is 50%

$$Q_{\text{required}} = \frac{0.6 \times 96500}{\frac{50}{100}} = \frac{0.6 \times 96500 \times 100}{50} = 115800 \text{ C}$$

(Q) If the potential drop in above ques is 3 V then find the maximum work done. (electrical work done)

Soln $W_{\text{electrical}} = Q \cdot V = (115800 \times 3) \text{ Joules}$

** GALVANIC CELL :-



Galvanic cell is a device in which chemical energy is converted into electrical energy.

In this a spontaneous redox rxn takes place.

The flow of current in external circuit is from cathode to anode, therefore, cathode is known as positive electrode and anode is known as negative electrode.

The flow of current in internal circuit is from anode to cathode.

** Salt Bridge -

Contains strong electrolyte in gel form (containing agar-agar).

These type of electrolytes are taken in salt bridge which do not react with electrolytic solutions as well as electrolytes.

ex. KCl, NH₄Cl, NH₄NO₃, KNO₃, etc.

Also, the ionic speed of cation or anion of electrolyte should be equal otherwise junction potential will develop.

** Role of Salt Bridge -

It completes the circuit.

It maintains the electrical neutrality.

It reduces the junction potential.

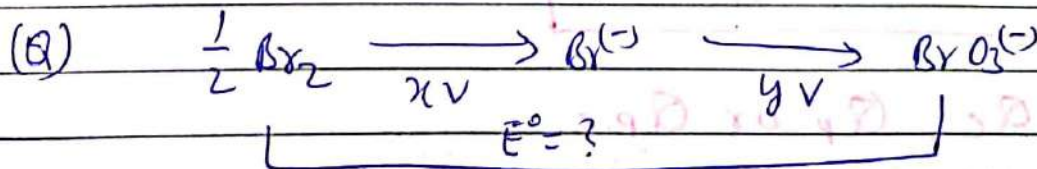
** Junction potential reduces the net EMF.

Standard electrode potential is an intensive property (non-additive).

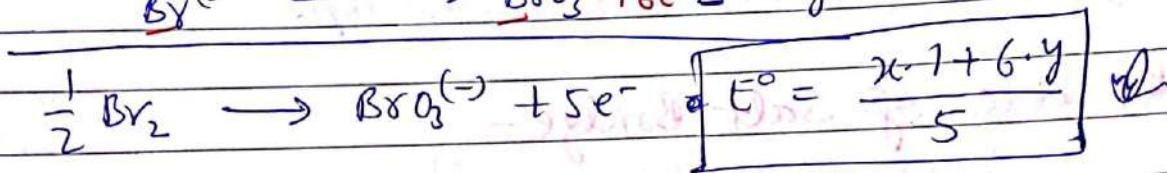
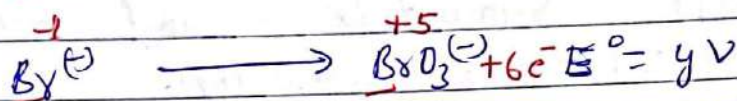
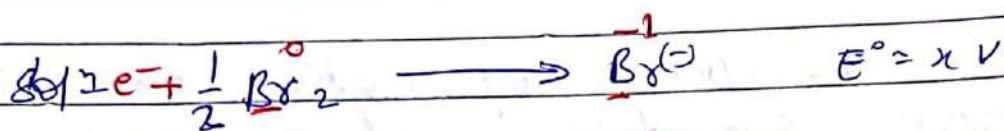
$$E_3^0 = \frac{n_1 E_1^0 + n_2 E_2^0}{n_3}$$

** Agar half-cell ke reaction ko bina e barabar kiyae add karne aur net reaction mein electron ke darshan ho jaye to kabhi bhi emf ko add nahi karne. Uss case me upar likhe gaye result ko use karne.

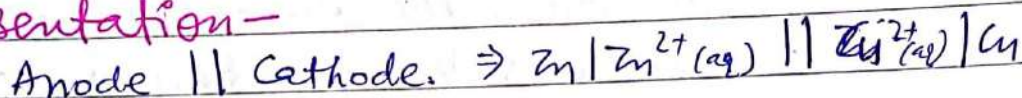
** If in galvanic cell, Zn electrode acts as anode and Cu acts as cathode then it is called Daniell cell.



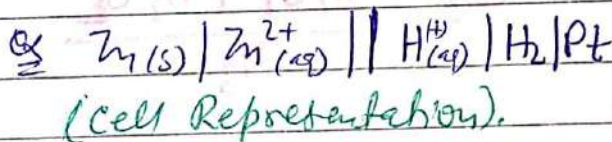
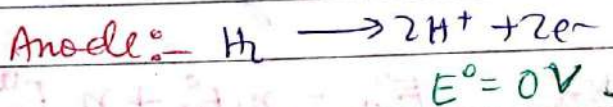
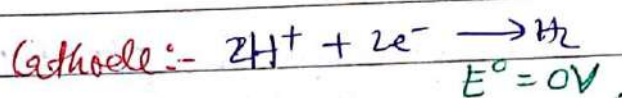
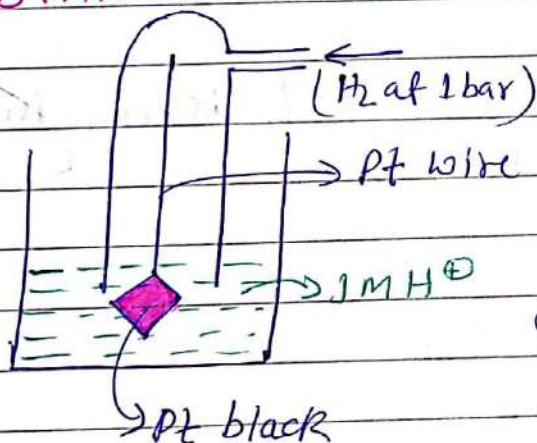
Solⁿ (in next page) →



Cell Representation -



STANDARD HYDROGEN ELECTRODE - (SHE) -



(Q) Represent a cell using Ni electrode and SHE.
solⁿ $\text{Ni}(s) | \text{Ni}^{2+}(\text{aq}) || \text{H}^+(\text{aq}) | \text{H}_2 | \text{Pt}$

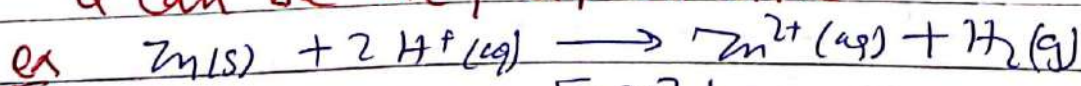
NERNST EQUATION:-

$$\Delta G = \Delta G^\circ + 2.303RT \log Q$$

$$\Rightarrow -nFE = -nFE^\circ + 2.303RT \log Q \Rightarrow E = E^\circ - \frac{2.303RT}{nF} \log Q$$

$$\Rightarrow E = E^\circ - \frac{0.0591}{n} \log Q$$

Q can be Q_c , Q_p or $Q_{p.c}$

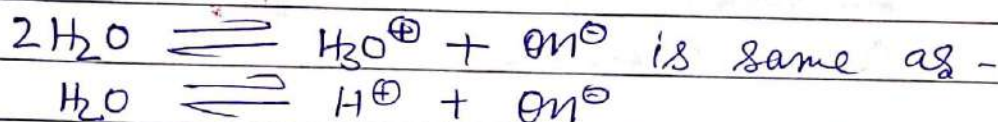


$$Q = Q_{p.c} = \frac{[\text{Zn}^{2+}] p_{\text{H}_2}}{[\text{H}^+]^2}$$

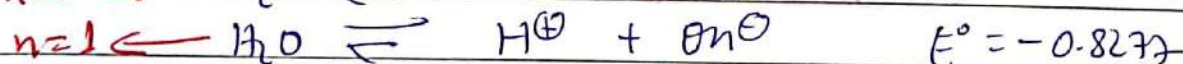
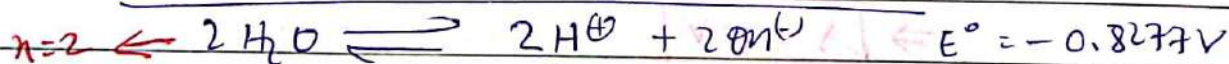
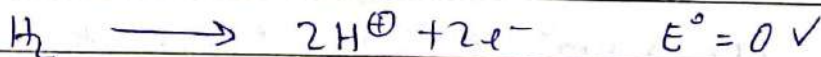
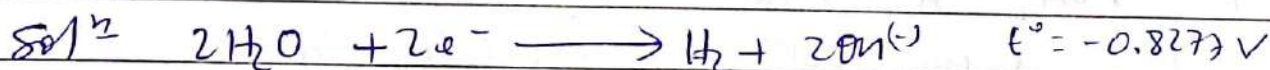
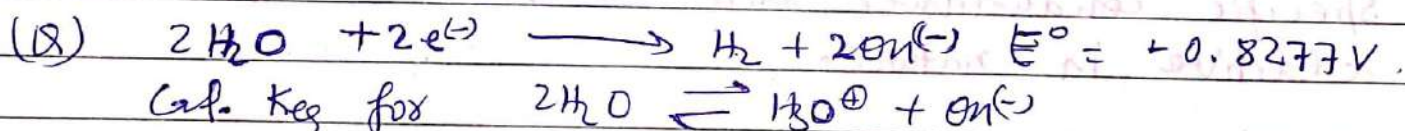
$\Delta G < 0 \Rightarrow$ Spontaneous $\Rightarrow E_{cell} > 0$ for spon. rxn.
(Do not use ΔG° or E°_{cell})

If $\Delta G > 0$ then this does not mean that cell won't work at all, it simply means that the polarity is to be reversed for cell to work or the rxn is spontaneous in backward dirⁿ.

$$E^\circ_{cell} = \frac{0.0591}{n} \log K_{eq} \quad (\text{At equm, } E_{cell} = 0)$$



No. of e^- transfer in $2H_2O \rightleftharpoons 2H^+ + 2OH^-$ is 2 while that in $H_2O \rightleftharpoons H^+ + OH^-$ is 1.



$$\therefore -0.8277 = \frac{0.0591}{1} \log K_{eq} \Rightarrow \log K_{eq} \approx -14$$

$$\Rightarrow K_{eq} = 10^{-14}$$

☆☆ Conductance -

Electronic Conductance (Metal conductance)

- * Due to movement of e^-
- * On \uparrow temp, \downarrow es
- * No mass transfer occurs.

Electrolytic Conductance -

- * ~~Conduct~~ Due to movement of ions.
- * On \uparrow temp, \uparrow es.
- * Mass Transfer occurs.

K : specific conductance or conductivity.

$$K = \frac{G \cdot L}{A}$$

L : Distance b/w electrodes

A : Area of cross-section of electrodes.

G : Conductance. $= (1/R)$

Note:- Agar do electrode ki area alag-alag hai to common area lete hai.

* Specific conductance and conductance are additive in nature. (extensive property).

If $L = 1 \text{ cm}$, $A = 1 \text{ cm}^2$ then $G = K$.

Thus, for $1 \text{ cm}^3 \text{ vol}^m$ of electrolyte, $G = K$

\Rightarrow For $V \text{ cm}^3 \text{ vol}^m$ of electrolyte, $G = KV$.

$$\Rightarrow \boxed{\lambda = KV} \quad \lambda: \text{Conductance.}$$

Note-① On dilution, conductance increases.

Reason \rightarrow on dilution α increases so no. of ions increases so \Rightarrow conductance (λ) \uparrow es.

② On dilution, no. of ions per unit volume decreases therefore specific conductance (K) decreases.

* Molar Conductance - All the conductance produced by 1 mole electrolyte is known as molar cond.

If Molarity = M

\Rightarrow Vol^m of M mol electrolyte = 1000 cm^3 .

\Rightarrow Vol^m of 1 mol electrolyte = $\frac{1000}{M} \text{ cm}^3$

$$\therefore \lambda = KV \Rightarrow \lambda_m = \frac{1000 \times K}{M} \quad \text{Unit} \rightarrow \text{Scm}^2 \text{ mol}^{-1}$$

* Equivalent Conductance - All the conductance produced by 1 gram equivalent of electrolyte.

If Normality = N

\Rightarrow Vol^m of N gram-equivalent = 1000 cm^3 .

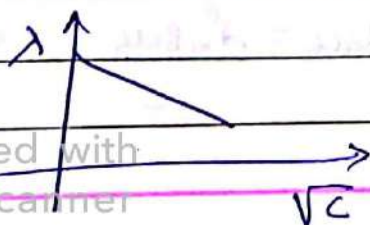
\Rightarrow Vol^m of 1 gram-equivalent = $\frac{1000}{N} \text{ cm}^3$.

$$\Rightarrow \lambda_e = \frac{K \times 1000}{N} \quad \text{Unit} \rightarrow \text{Scm}^2 / \text{equivalent}$$

$$\lambda_m = n\text{-factor} \times \lambda_e$$

** Conductance at infinite dilution - (λ^∞ or λ^0)
Maximum conductance of any electrolyte.
It is also called limiting molar conductance.

** Variation of conductance of strong electrolyte with concentration - $\lambda = \lambda^0 - A\sqrt{C}$



$A = \text{constant}$

(depends on temp^o and nature of electrolyte)

* At infinite dilution, weak electrolyte behaves as strong electrolyte.

* Degree of ionisation of weak electrolyte.

$$\lambda^{\circ} \longrightarrow \alpha = 1$$

$$\lambda^{\circ} \longrightarrow \alpha = \frac{\lambda^c}{\lambda^{\circ}}$$

$\alpha = \frac{\lambda^c}{\lambda^{\circ}}$

* Kohlrausch's law :-

A/c to Kohlrausch's law, the equivalent conductance of any electrolyte at infinite dilution is equal to sum of equivalent conductance of cation and anion.

ex $\lambda^{\circ} \text{Al}_2(\text{SO}_4)_3 = \lambda^{\circ} \text{Al}^{3+} + \lambda^{\circ} \text{SO}_4^{2-}$

$$\lambda_m^{\circ} \text{Al}_2(\text{SO}_4)_3 = 2 \lambda_m^{\circ} \text{Al}^{3+} + 3 \lambda_m^{\circ} \text{SO}_4^{2-}$$

** Application of Kohlrausch's law -

(1) Calculation of conductance at infinite dilution -

(2) $\lambda_m^{\circ} \text{BaSO}_4 = x$, $\lambda^{\circ} \text{HCl} = y$, $\lambda_m^{\circ} \text{H}_2\text{SO}_4 = z$
Find $\lambda^{\circ} \text{BaCl}_2$.

Soln $\lambda_m^{\circ} \text{BaCl}_2 = \lambda_m^{\circ} \text{Ba}^{2+} + 2 \lambda_m^{\circ} \text{Cl}^-$

$$\lambda_m^{\circ} \text{BaCl}_2 = \lambda_m^{\circ} \text{BaSO}_4 - \lambda_m^{\circ} \text{H}_2\text{SO}_4 + 2 \lambda_m^{\circ} \text{HCl}$$

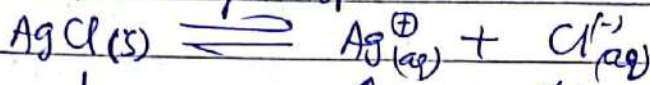
$$\Rightarrow \lambda_m^{\circ} \text{BaCl}_2 = x - z + 2y \Rightarrow \lambda^{\circ} \text{BaCl}_2 = \frac{\lambda_m^{\circ} \text{BaCl}_2}{2} = \frac{x - z + 2y}{2}$$

(1) Compare λ of Li^+ , Na^+ , K^+ :

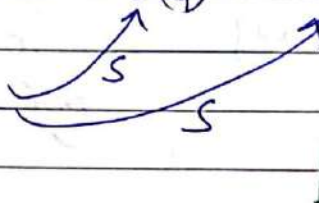
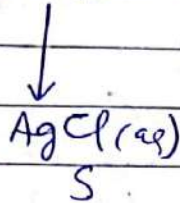
Solⁿ $\text{K}^+ > \text{Na}^+ > \text{Li}^+$ (size in gas phase).
 $\text{K}^+ < \text{Na}^+ < \text{Li}^+$ (size in aqueous phase). } $\Rightarrow \lambda(\text{KCl} > \text{NaCl} > \text{LiCl})$

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(2) Calculation of K_{sp} .



$$K_{\text{AgCl}} = K_{\text{soln}} - K_{\text{H}_2\text{O}}$$



$$\lambda_{\text{AgCl}}^{\circ} = K_{\text{AgCl}} \times \frac{1000}{S}$$

(Since at infinite dilution, $m = S$).

$$K_{sp} = S^2$$

Important

$$\lambda_{\text{m Ag}_3\text{PO}_4(s)}^{\circ} = K_{\text{Ag}_3\text{PO}_4} \times \frac{1000}{S}$$

$$\lambda_{\text{e Ag}_3\text{PO}_4(s)}^{\circ} = K_{\text{Ag}_3\text{PO}_4} \times \frac{1000}{N} - K_{\text{Ag}_3\text{PO}_4} \times \frac{1000}{3S}$$

~~IX~~ Ionic mobility: (μ) -

Distance travelled by any ion in 1 sec under unit potential gradient. ($\frac{dV}{dx} = 1 \text{ V/m}$)

Conductance (λ) \propto Ionic mobility (μ) $\Rightarrow \lambda \propto \mu$ or, $\lambda = F\mu$

F : Faraday = 96500 C

~~IX~~ Transport No: (t) -

It is the fraction of total current carried by cation or anion.

$$t_{\oplus} + t_{\ominus} = 1 \quad t_{\oplus} = \frac{\mu_{\oplus}}{\mu_{\oplus} + \mu_{\ominus}} \quad \text{or,} \quad t_{\ominus} = \frac{\mu_{\ominus}}{\mu_{\oplus} + \mu_{\ominus}}$$

$$t_{\oplus} = \frac{\lambda_{\oplus}}{\lambda_{\oplus} + \lambda_{\ominus}} \quad \text{or,} \quad t_{\ominus} = \frac{\lambda_{\ominus}}{\lambda_{\oplus} + \lambda_{\ominus}}$$

* In case of ions (cations + ions), H^+ ion has max. conductance.

* While, in case of anions, OH^- has max. conductance.

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