

11/05/2022

UNIT - 1

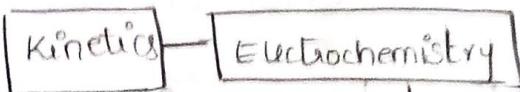
ELECTRODICS & ITS APPLICATIONS

* Electrodics:

Conversion of electrical energy

to chemical energy (or) vice versa.

is done with the help of electrochemistry.



Thermodynamics

* CHEMICAL ENERGY to ELECTRICAL ENERGY:

Sub-Topics:

- 1) Conductance
 - 2) Electrodes
 - 3) Applications in
chemical analysis.
- & related applications

* CONDUCTANCE:

Materials can be classified into 4 types based on conductivity:

- 1) Conductors: conduct electricity
- 2) Insulators: do not conduct electricity
- 3) Super conductors: conduct at curie temp.
- 4) Semiconductors: conduction takes place when it is doped.

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Types of conductors:

- Metallic (electronic).: e⁻s are available - solids.
Ex: Metals.
- electrolytic (Ionic).: ions are responsible - Liquids.

* Metallic conductors & Electrolytic conductors obeys Ohm's Law.

$$V = IR$$

* When temp ↑ses in metallic conductor, resistance ↑ses and conductance ↓ses

* When temp ↑ses in electrolytic conductor, degree of dissociation ↑ses; ions for conduction ↑ses; hence conduction ↑ses.

⇒ Electrolyte: A substance which gives ions on dissociation in a suitable solvent are called electrolytes.

Types: Strong and Weak electrolyte.

Strong electrolyte: Degree of dissociation is almost equal to 1. Ex: strong acids, strong bases.

Weak electrolyte: Degree of dissociation is smaller than 1. Ex: weak acids.

** already written

* Differentiate between Metallic and Electrolytic conductors.

* Resistance: Opposition to the flow of e⁻s in a material [Units = Ω (ohm)]

* Conductance: Allows the flow of e⁻s in a material

[Units = mho (ohm⁻¹)]

* Electrodes are generally made up of platinum, since it is inert in nature.

→ Top surface of electrolytic plates is coated with platinum black.

To avoid reaction with other elements/molecules

Platinum black also increases its sensitivity/response rate

let l = distance between the plates
 A = area of cross section of plates

$$\text{Cell constant} = \frac{l}{A}$$

units : cm⁻¹

$$R = \frac{\rho l}{a}$$

Specific Conductance (K)

conductance offered by 1cc solⁿ.

$$K = \frac{1}{R} \cdot \frac{l}{a}$$

R = resistance offered by solⁿ.

$$R \propto l$$

$$\propto \frac{1}{a}$$

$$R = \frac{\rho l}{a}$$

$$\frac{l}{a} \cdot \frac{1}{K} = \frac{1}{\rho} R$$

$$K = \frac{1}{R} \cdot \frac{l}{a}$$

where ρ = resistivity

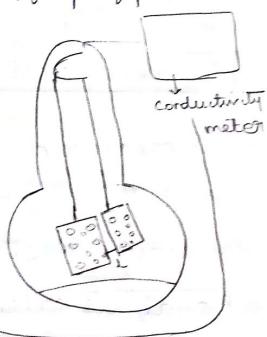
$$K = \frac{1}{\rho} = \text{conductivity}$$

units of ρ = Ω m

$$\text{units of } K = \Omega^{-1} m^{-1}$$

= Si m⁻¹

= S m⁻¹



$$K = G \frac{l}{a}$$

$K = G \times \text{cell const}$

$$\text{at } \frac{l}{a} = 1 \text{ cm}^{-1}$$

$$K = G \\ P = R$$

* The measured conductance of an electrolytic solⁿ when it is placed b/w 2 electrodes separated by unit length and area unit ~~area~~ across-sectionally is called specific conductance.

* Molar Conductance: (λ_M)

- Conductance is measured with respect to molarity.

$$[\text{S} \cdot \text{cm}^2 \cdot \text{mole}^{-1}] \quad \lambda_M = \frac{1000 \times K}{M}$$

* Equivalent Conductance:

- Conductance is measured with respect to normality.

$$[\text{S} \cdot \text{cm}^2 \cdot \text{eq}^{-1}] \quad \lambda_{\text{eq}} = \frac{1000 \times K}{N}$$

With dilution i.e. Volume \uparrow ses, conc. \downarrow ses.

$1 \text{M sol}^n \Rightarrow 1 \text{GMwt dissolved in 1L}$

$\Rightarrow 1 \text{mole}$

Conductance offered by 1M electrolytic solution is molar conductance.

Conductance offered by 1N electrolytic solution placed between 2 electrodes is called equivalent conductance.

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Molarity = Normality if [nfactor = 1]

* Calculate cell constant a which is used to measure conductance of KCl solⁿ. Resistance found to be 50Ω and conductivity is $1.5 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$

$$R = 50 \Omega$$

$$K = \frac{1}{R} \frac{l}{a}$$

$$\text{cell constant} = 15 \times 10^{-3}$$

$$\frac{l}{a} = 15 \times 10^{-3} \text{ cm}^{-1}$$

* $A = 5 \text{ cm}^2$ and they are separated by 10cm apart in a conductivity cell that offered 125 Ω resistance for KCl solⁿ at 25°C . Calculate conductivity.

$$K = \frac{1}{R} \frac{l}{a} \\ = \frac{1}{125} \times \frac{10}{5}$$

$$K = 16 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$$

* Specific conductivity of 0.1M NaCl solⁿ is $3.4 \times 10^{-2} \Omega^{-1}\text{cm}^{-1}$. Resistance offered by the same solⁿ is 80Ω at 25°C. The same cell is used for KCl solⁿ which offered 50Ω resistance. Calculate specific conductance of solⁿ.

$$K = G \frac{l}{a}$$

$$K_1 = 3.4 \times 10^{-2}$$

$$K_2 = ?$$

$$R_1 = 80 \Omega$$

$$R_2 = 50 \Omega$$

$$K \propto \frac{1}{R}$$

$$\frac{K_1}{K_2} = \frac{R_2}{R_1} \quad K_2 = \frac{K_1 R_1}{R_2} = 5.44 \times 10^{-2} \Omega^{-1}\text{cm}^{-1}$$

* Calculate molar conductance & equivalent conductance of AgCl solⁿ of 0.1M at 25°C. cell constant is $1.0 \Omega^{-1}\text{cm}^{-1}$ and resistance is 20Ω

$$\begin{aligned} \lambda_M &= \frac{1000}{M} \times \frac{1}{R} \times \frac{l}{a} \\ &= \frac{1000}{0.1} \times \frac{1}{20} \times 1.0 = 500 \text{ S cm}^2 \text{ mole}^{-1} \end{aligned}$$

$$\begin{aligned} \lambda_{eqv} &= \lambda_M \quad \because M = N \\ &= 500 \text{ S cm}^2 \text{ mole}^{-1} \end{aligned}$$

* CONDUCTOMETRIC TITRATION: (only electrolyte)

- 1) Strong acid vs Strong Base
(HCl vs NaOH)
 - 2) Weak acid vs Strong Base.
(CH₃COOH vs NaOH)
 - 3) Mix. of acids vs Strong Base.
(HCl + CH₃COOH vs NaOH)
-

* Factors affecting titrations: / conductance of solⁿ.

- 1) Nature of electrolyte → S.E ($\alpha \approx 1$)
 - 2) Solvent - viscosity → W.I.E ($\alpha \ll 1$)
 - 3) Temperature
 - 4) Concentration/ no. of ions
 - 5) Mobility of ions.
- viscous solⁿ = resistance to flow.

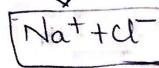
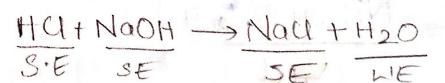
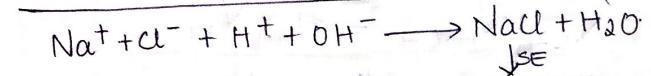
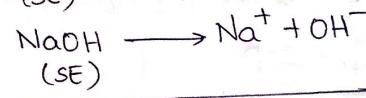
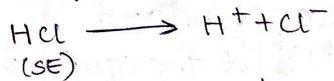
Galvanic cell:
anode (-)
cathode (+)

electrolytic cell:
anode (+)
cathode (-)

* Applications:

chemical analysis.
Qualitative
Quantitative

* Strong Acid vs Strong Base:

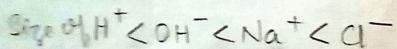


WE

No. of ions in the beaker remains same
But no. of H^+ ions $\text{NaOH} \rightarrow$
decreases.

$\because Na^+$ is heavier than H^+ ∴ mobility of ions decreases; thereby conductance is decreased by the time titration is completed - it becomes minimum.

Till the point at which HCl is completely neutralised no. of ions decreases but after that no. of ions increases and hence conductance increases.



Conductance Offered : $H^+ > OH^- > Na^+ > Cl^-$

The volume at which the standard solution is neutralised ^{by a base} is at the equivalence point.

$$V_{\text{NaOH}} = e.p.$$

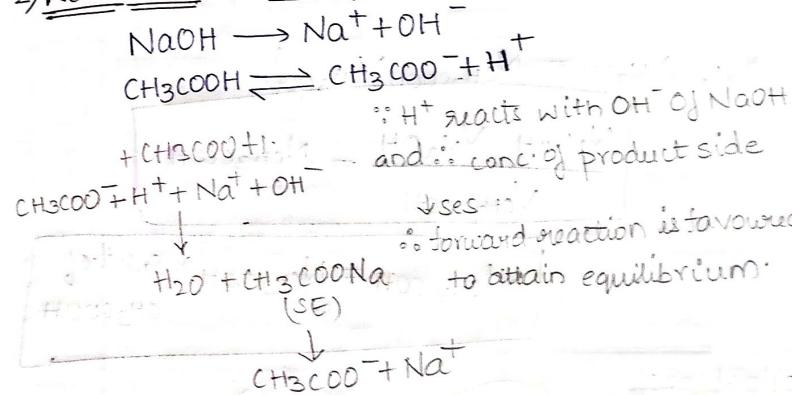
$$N_{\text{NaOH}} V_{\text{NaOH}} = N_{\text{HCl}} V_{\text{HCl}}$$

$$N_{\text{HCl}} = \frac{N_{\text{NaOH}} V_{\text{NaOH}}}{V_{\text{HCl}}}$$

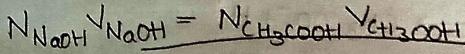
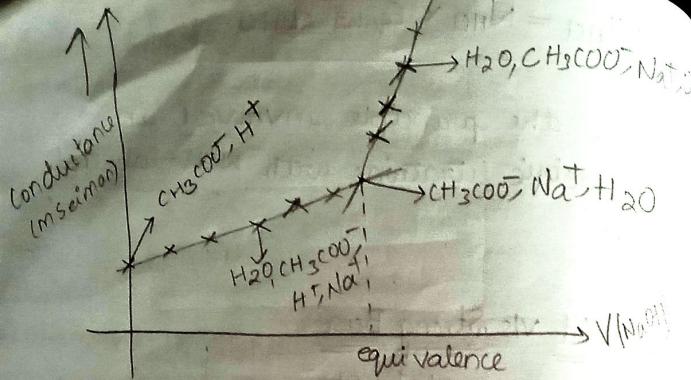
$$W_{\text{HCl}} = N_{\text{HCl}} \times \text{eq. wt of HCl}$$
GL

* Describe the principle involved in conductometric titrations with well-labelled diagram.

2) Weak Acid vs Strong Base:



After the neutralisation of CH_3COOH , there are only Na^+ & OH^- ; where OH^- will cause a step increase in conductance. Before neutralisation is attained, the salt CH_3COONa (SE) formed dissociates into CH_3COO^- & Na^+ and also the molecule CH_3COOH favours forward reaction ~~due~~ so as to attain equilibrium.



$$\frac{N_{\text{NaOH}} V_{\text{NaOH}}}{V_{\text{CH}_3\text{COOH}}} = N_{\text{CH}_3\text{COOH}}$$

$$Wt_{\text{CH}_3\text{COOH}} = N_{\text{CH}_3\text{COOH}} \times \text{Eq wt. of CH}_3\text{COOH}$$

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3) Mixture of acids v/s Strong Base:

* Common ion effect decreases the dissociation of weak acid.

T* COMMON ION EFFECT:



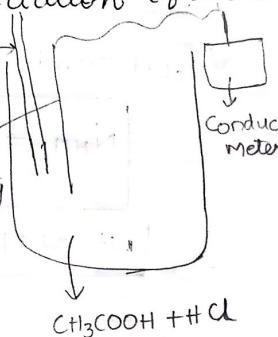
Due to common ion effect; HCl undergoes dissociation first.

g. HCl and CH_3COOH are mixed together, which acid will undergo neutralisation first? Why?

* Common ion effect is defined as the common ion formed when a strong acid and a weak acid are mixed; the dissociation of weak acid is suppressed.

* HCl undergoes neutralisation initially whereas CH_3COOH do not undergo neutralisation due to common-ion effect.

i.e. neutralisation of CH_3COOH (WA) is suppressed.



Conductance (ms)

HCl

$\text{CH}_3\text{COO}^- + \text{H}^+$

0

a

b V NaOH (ml)

* Once HCl is neutralised completely; the solution in the beaker acts as a pure acetic acid solⁿ; wherein; the conductance gradually increases.

$$a = V_{\text{NaOH}} \text{ required to neutralise HCl}$$

$$b = V_{\text{NaOH}} \text{ required to neutralise mix}$$

$$b-a = V_{\text{NaOH}} \text{ required to neutralise CH}_3\text{COOH}$$

$$(NV)_{NaOH} = (NV)_{HCl}$$

N_{NaOH} = known

V_{NaOH} = ml

$$N_{HCl} = ?$$

$\checkmark N_{HCl}$ known.

$$N_{HCl} = \frac{(NV)_{NaOH}}{V_{HCl}}$$

$$\text{wt. of HCl} = N_{HCl} \times 36.5 \text{ g/L}$$

$$(NV)_{NaOH} = (NV)_{CH_3COOH}$$

N_{NaOH} = known

$$N_{CH_3COOH} = ?$$

$V_{NaOH} = (b-a) \text{ ml}$

$\checkmark CH_3COOH$ = known

$$N_{CH_3COOH} = \frac{(NV)_{NaOH}}{V_{CH_3COOH}}$$

$$\text{wt. of } CH_3COOH = N_{CH_3COOH} \times 60 \text{ g/L}$$

Describe the principle involved in any 2 conductometric titrations with a neatly labelled graph

$\Delta A \Rightarrow$ workfn \Rightarrow used when there were volume changes

$\Delta G \Rightarrow$ Gibbs energy \Rightarrow used when there is energy change

* TYPES OF CELLS

ELECTRODICS:

* TYPES OF CELLS:

1) Electrolytic

2) Electrochemical (Galvanic) Cells.

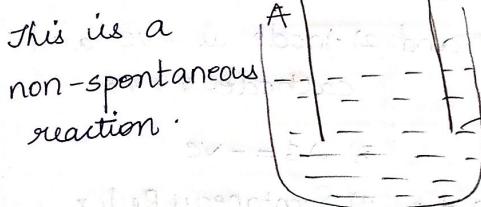
* Cell is a device which converts chemical energy to electrical energy and vice versa.

* In electrolytic cell; using electrical energy a reaction is performed.

- Change in Gibbs free energy
 $\Delta G = +ve$

Redox Reaction

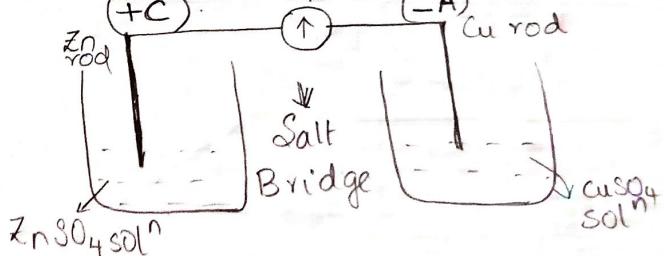
electrolytic solⁿ.



* GALVANIC CELLS:

In this type of cell; chemical energy is converted to electrical energy. $\Delta G = -ve$

- Spontaneous Redox Reaction



• Cell contains 2 electrodes (2 half-cells, anode & cathode). In this device it is E to EE (or) vice versa.

- Salt Bridge connects the 2 half-cells in a Galvanic Cell.

* Differentiate b/w electrolytic & galvanic

ELECTROLYTIC:

- 1) Converts electrical energy to chemical energy
- 2) Anode is +ve and cathode is -ve
- 3) $\Delta G = +ve$
- 4) Non-Spontaneous Redox Reaction
- 5) Both half cells are placed in same beaker, without salt bridge

GALVANIC:

- 1) Converts chemical energy to electrical energy
- 2) Anode is -ve, cathode is +ve
- 3) $\Delta G = -ve$
- 4) Spontaneous Redox Reaction
- 5) Salt Bridge connects the 2 half cells placed in 2 different solutions

02/06/2022

* CONCEPT OF ELECTRODE POTENTIAL:

→ cell containing 2 half-cells naming anode & cathode which undergoes REDOX reaction.

* When a metal rod placed in the solution of same metal undergoes dissolution and deposition.

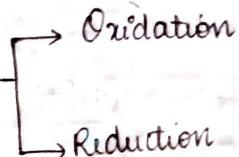
→ Dissolution: When there is a change in concentration of ions in the solution
→ if ions from rod are released into sol⁺ it is called DISSOLUTION.

→ if ions from sol⁺ are deposited on rod it is called DEPOSITION.
At equilibrium attained by the setup:

$$\frac{\text{Rate of dissolution (oxidation)}}{\text{Rate of deposition (reduction)}} = \frac{\text{Rate of deposition (reduction)}}{\text{Rate of oxidation}}$$

* Measurement of tendency of a metal rod placed in same ionic solution to undergo either dissolution (or) deposition gives the ELECTRODE POTENTIAL (E)

* ELECTRODE POTENTIAL:



Standard Conditions:

If the ionic solution taken in the beaker is of 1M concentration and the temperature is 25°C ; the measured electrode potential (E) is called standard electrode potential (E°).

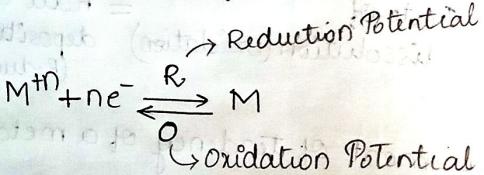
→ Standard Oxidation Potential (SOP)

→ Standard Reduction Potential (SRP).

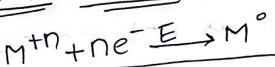
At anode: Oxidation takes place.

At cathode: Reduction takes place.

* Due to the production of electrode potential; the Galvanic cell undergoes spontaneous redox reaction.



* Reduction Potential:



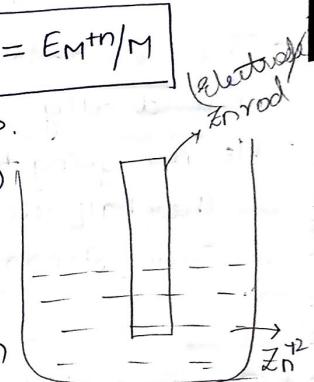
$$E_R = E_{\text{M}^{+n}/\text{M}}$$

$$E^\circ = E_{\text{M}^{+n}/\text{M}} \rightarrow \text{SRP.}$$

* Based on nature of metal rod (or) the electrolytic (ionic) solution; initially it may undergo either oxidation or reduction.

* But after sometime; equilibrium is attained where:

$$\text{Rate of Oxidation} = \text{Rate of Reduction}$$



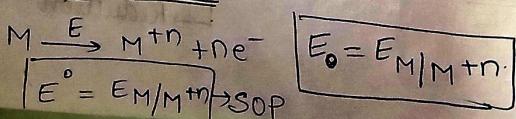
* Measure of tendency of an electrode to undergo oxidation when the rod is placed in corresponding ionic solution is called OXIDATION POTENTIAL.

* Measure of tendency of an electrode to undergo reduction when the rod is placed in corresponding ionic solution is called REDUCTION POTENTIAL.

→ Measure of tendency of an electrode to undergo oxidation when the rod is placed in corresponding 1M ionic solution at 25°C is called Standard Oxidation Potential.

→ Measure of tendency of an electrode to undergo reduction when the rod is placed in corresponding 1M ionic solution at 25°C is called Standard Reduction Potential.

* Oxidation Potential:



$$E^\circ = E_{\text{M}/\text{M}^{+n}} \rightarrow \text{SOP}$$

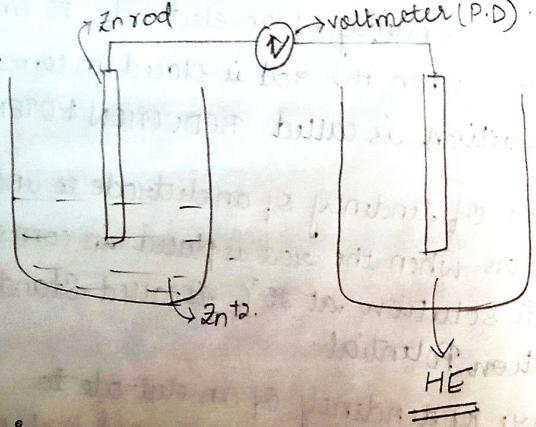
$$E^\circ = E_{\text{M}/\text{M}^{+n}}$$

* Can we determine single electrode potential?
⇒ Single electrode potential is not measured individually.

∴ We are going to connect the given rod with another half-cell i.e. primary reference electrode [Standard Hydrogen Electrode (0V)] to complete the construction (or) HE of cell

* Potential difference developed in the above setup; is called the electrode potential of rod (E) connected.

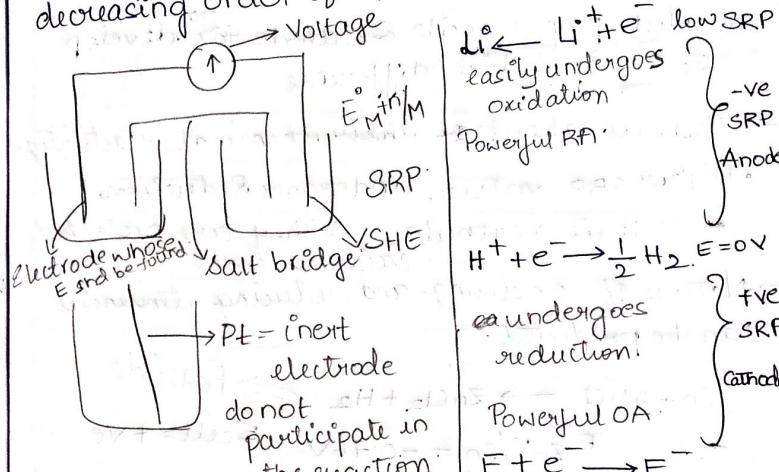
- $E = +ve$: SHE is anode
connected electrode is cathode
- $E = -ve$: SHE is cathode
connected electrode is anode.



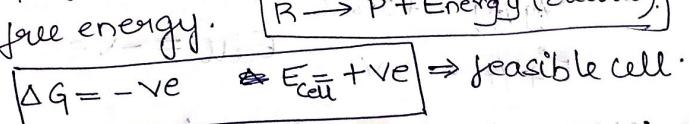
* If primary reference electrode is standard hydrogen electrode; then potential developed is standard electrode potential.

Electrochemical Series and Applications: 03/06/22

* It is a series in which the elements are arranged according to either increasing (or) decreasing order of their SRPs.



$\Delta G = -ve$: the system has some initial energy (internal energy) which is utilized to perform a work. This energy is called free energy.

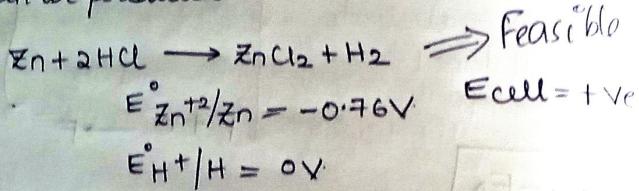


* Standard Reduction Potentials of electrodes is arranged in increasing order.

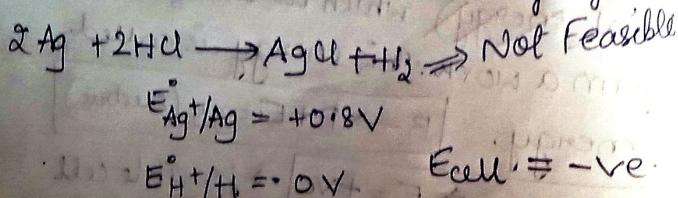
* All the ~~series~~ batteries are generally made up of lithium ion since voltage is maximum.

APPLICATIONS:

- Helps in constructing a feasible cell or to select proper anode & cathode for development.
- ($E_{cell} = +ve$) potential difference.
- Tells us about their chemical reactivity.
- Higher SRP value; undergoes Reduction.
- \because it is a cathode \therefore they are products.
- \therefore Oxidising Agent.
- Nature of oxidising and reducing tendencies can be predicted.



• Lower SRP value; undergoes oxidation.
 \because it is anode \therefore Reducing agent



→ Predict the feasibility of a redox reaction.

→ E_{cell} can be calculated from electrochemical series.

CELL NOTATION:

* Can we store $CuSO_4$ solⁿ in Zn container?

$$E^\circ_{Zn/Zn^{+2}} = +0.76V \quad E^\circ_{Cu/Cu^{+2}} = -0.34V$$

$$E^\circ_{SO_4^{2-}/SO_4} = 0.76V \quad E^\circ_{SO_4^{2-}/SO_4} = -0.34V$$

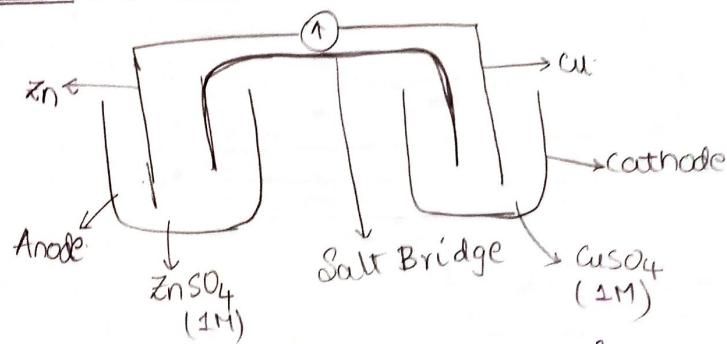
$$E^\circ_{SRP} = -0.76V \quad E^\circ_{SRP} = 0.34V$$

No; we can store $CuSO_4$ solⁿ in Zn container because Cu is deposited on the container.

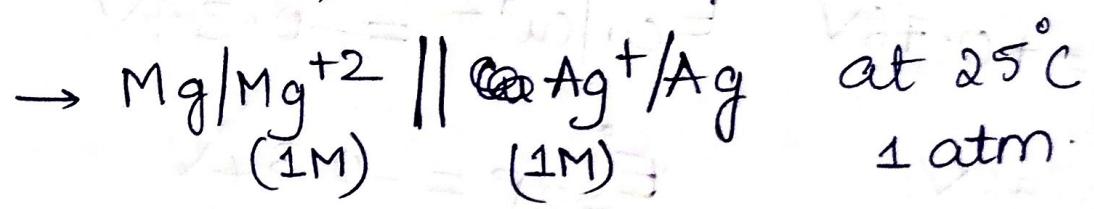
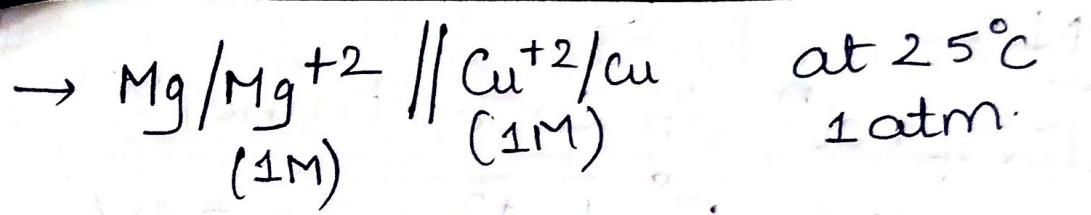
* Can we use Mg spatula to stir $AgCl$ solution?

$$E^\circ_{Mg}$$

CELL NOTATION:



IUPAC: $Zn/Zn^{+2} \parallel Cu^{+2}/Cu^0$ at $25^\circ C$ 1 atm



* NERNST EQUATION: