# ELECTROCHEMISTRY

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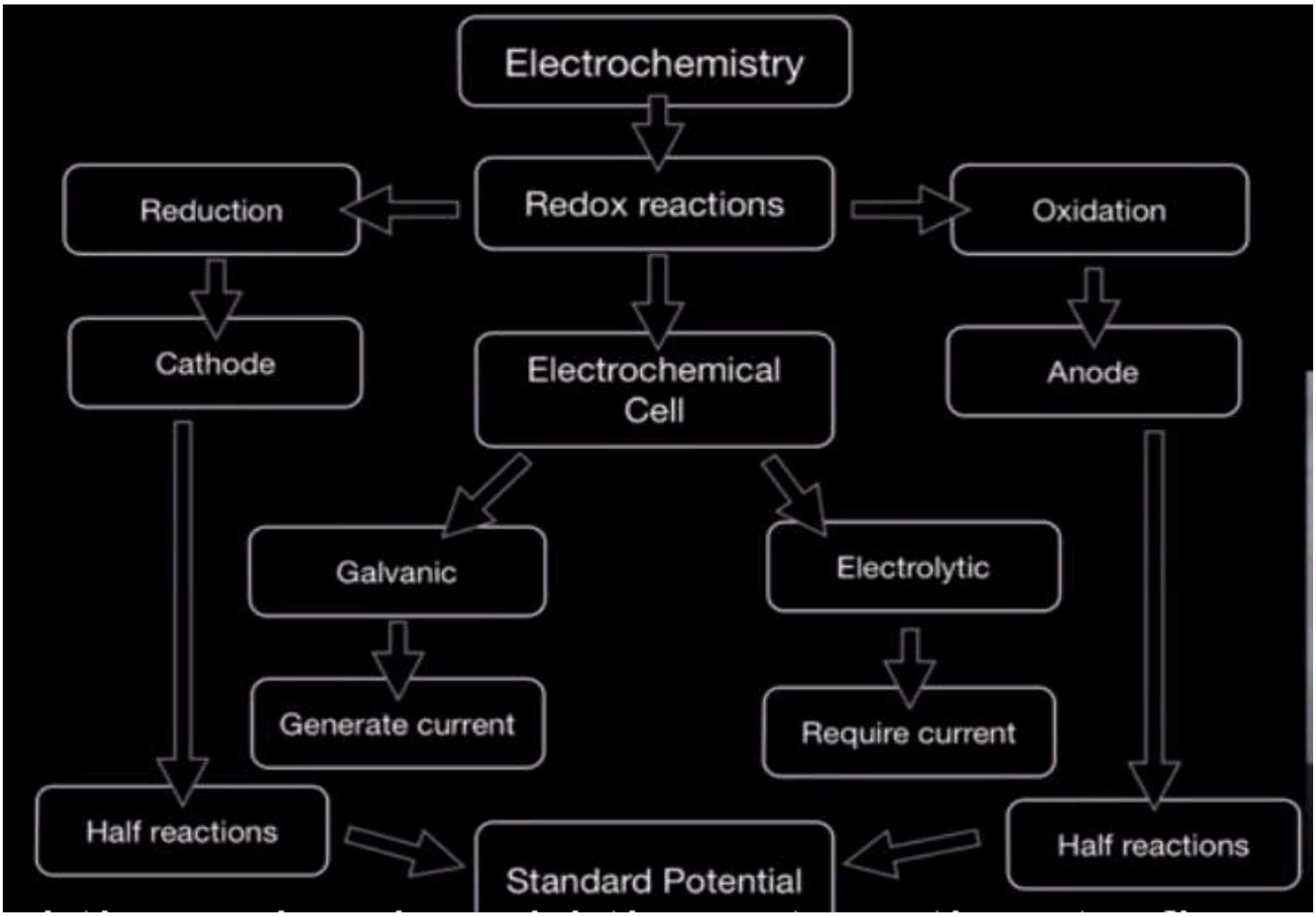
***Electrochemistry is a branch of chemistry which deals with an inter-conversion of chemical and electrical energies.***


Electrochemistry
Redox reactions
Reduction
Oxidation
Cathode
Electrochemical Cell
Anode
Galvanic
Electrolytic
Generate current
Require current
Half reactions
Standard Potential
Half reactions

# REDOX REACTION

- To generate current or moving electron by carrying out REDOX Reactions in an electrochemical cell.

- REDOX Reaction is a combination of :

(i) Oxidation reaction (lose of electron)

(ii) Reduction reaction (gain of electron)

Q.1 Whether the given reaction is oxidation or reduction reaction?

$$S_2O_3^{-2} = S_4O_6^{-2}$$

$$SO_4^{-2} = S_2O_8^{-2}$$

- An *electrochemical cell* can be defined as a single arrangement of two electrodes in one or two electrolytes which converts chemical energy into electrical energy or electrical energy into chemical energy.

$\Delta G^O = -nFE^0$

$\Delta G^O$ = The amount of free energy released (negative $\Delta G$) or absorbed (positive $\Delta G$) in a reaction in standard condition i.e.

P= 1atm; $Conc^n$ = 1M; Temp= $25^O$C

"n" = No. Of moles of electrons involved in REDOX Reaction

"F" = Quantity of charge in Faraday

"$E^O$" = Standard Electrode Potential

1F = 96500 coulomb (C) i.e . Amt. Of charge carried by one mole of electron

# FREE ENERGY CHANGE

Different equations of showing relationship as:

$\Delta G^O = \Delta H^O - T\Delta S^0$ ------------- (i)

$\Delta H^O$ = Standard Enthalpy change

$\Delta S^0$ = Standard Entropy change

$\Delta S = nF \{\Delta E / \Delta T\}_P$ ----------- (iii)

$\Delta G = \Delta G^O + RT\ln Q$ ----------- (iv)

$\Delta G$ = free energy at any point of time in a chemical change

$\ln Q$ = natural log of the reaction quotient

At equilibrium point; $\Delta G = 0$, So 'Q" = "K";

K = Equilibrium Constant

**Now, Equation becomes:**

$\Delta G^O = - RT\ln K$ or $\Delta G^O = - 2.303RT \log K$ (v)

## SPONTANEOUS AND NON-SPONTANEOUS CHANGE

| SPONTANEOUS CHANGE | NON-SPONTANEOUS CHANGE |
| --- | --- |
| $\Delta G < 0$ | $\Delta G > 0$ |
| $\Delta H < 0$ | $\Delta H > 0$ |
| $\Delta S > 0$ | $\Delta S < 0$ |
| $K > 0$ | $K < 0$ |
| $E > 0$ | $E < 0$ |

# TYPES OF ELECTROCHEMICAL CELL

- Electrochemical cells are of two types:

(i) Galvanic or voltaic cell
- Generate Current/Electron
- Example: Battery

(ii) Electrolytic cell:
- Require Current/Electron
- Example: Rechargeable Battery

# ELECTRODE POTENTIAL

- It measures the tendency of species to accept electron ( Reduction Potential , $E_{red}$) or to lose electron (Oxidation Potential , $E_{ox}$) when they are in contact with aqueous solution of their ion.
- In standard condition i.e. Concentration of solution 1M, temp. $25^0$c and Pressure 1 atm. it is termed as Standard Electrode Potential ($E^0$) Otherwise, it is termed as E.

- **Factors affecting El**ectrode Potential

(a) Sublimation of a solid metal

(b) Ionization Energy

(c) Hydration Energy

(d) Dissociation Energy

(e) Electron affinity

# ELECTROCHEMICAL SERIES

Less reactive

| Element | Reduction potential / V |
|---|---|
| Lithium | -3.04 |
| Potassium | -2.936 |
| Calcium | -2.868 |
| Sodium | -2.714 |
| Magnesium | -2.36 |
| Aluminum | -1.677 |
| Lead | -1.26 |
| Zinc | -0.762 |
| Iron | -0.44 |
| Cobalt | -0.282 |
| Nickel | -0.236 |
| Tin | -0.141 |
| Copper | 0.339 |
| Silver | 0.799 |
| Mercury | 0.852 |
| Platinum | 1.18 |
| Gold | 1.69 |

More reactive

# APPLICATIONS OF ELECTROCHEMICAL SERIES

**(a) To compare the strength of Oxidizing & Reducing agent:**

Q.2 Arrange the following in decreasing order of their strength as oxidizing agent: $F_2$ , $Cl_2$ $Br_2$

$E^0_{ox}$ for $F_2$ $Cl_2$ $Br_2$ are –2.87v, -1.36v & -1.06v respectively.

Q.3 Arrange the following in decreasing order of their strength as reducing agent: , Na , Ni & Pb.

$E^0_{red}$ for Na , Ni & Pb are – 2.7v , -0.25V & -0.13V respectively.

**(b) Decomposition of Hydra acid & water by a metal : Metals , above hydrogen in electrochemical series decompose hydra acids & water to give Hydrogen gas.**

Q.4 Which one will replace hydrogen from HCl?

Cu or Na

**(c) Displacement reaction :** Metal having higher –ve $E_{red}$ displace the metal of lower $E_{red}$ -ve from the solution.

$$Zn(s) + Cu_{(aq)}^{+2} = Cu(s) + Zn_{(aq)}^{+2}$$

**(d) Electroplating :** Metals having higher –ve $E_{red}$ are protected by the metal of lower $E_{red}$ -ve.

Q. 5 $E^0_{red}$ for Zn , Fe, Sn & Cu = -0.76v , -0.44v , -0.14v & 0.34v respectively. Whether Zn is protected by Sn or Fe?

**(e) Stability of Ion in solution.**

Q.6 Given that $E^0_{Cu^{+1}/Cu^{+2}} = -0.15V$ & $E^0_{Cu^{+1}/Cu} = 0.50V$. Calculate $E^0$ for disproportion reaction $2Cu^+ = Cu^{+2} + Cu$ ? Whether $Cu^+$ is stable in aq. solution or not?

(Ans:$E^{\varnothing}$=+0.37**V** Since $E^0$ is positive so $Cu^+$ disproportionate & not stable)

## REFERENCE ELECTRODES

### 1. Primary Reference Electrode

- **Standard Hydrogen Electrode (SHE)**

  ½ $H_{2\ (p=1atm)}$ | $H^{+}_{\ (c=1M)}$

  $E^0$ taken as 0.00 V at $25^0C$

### 2. Secondary Reference Electrodes

- Calomel electrode

  Hg| $Hg_2Cl_{2,}$ $Cl^-$

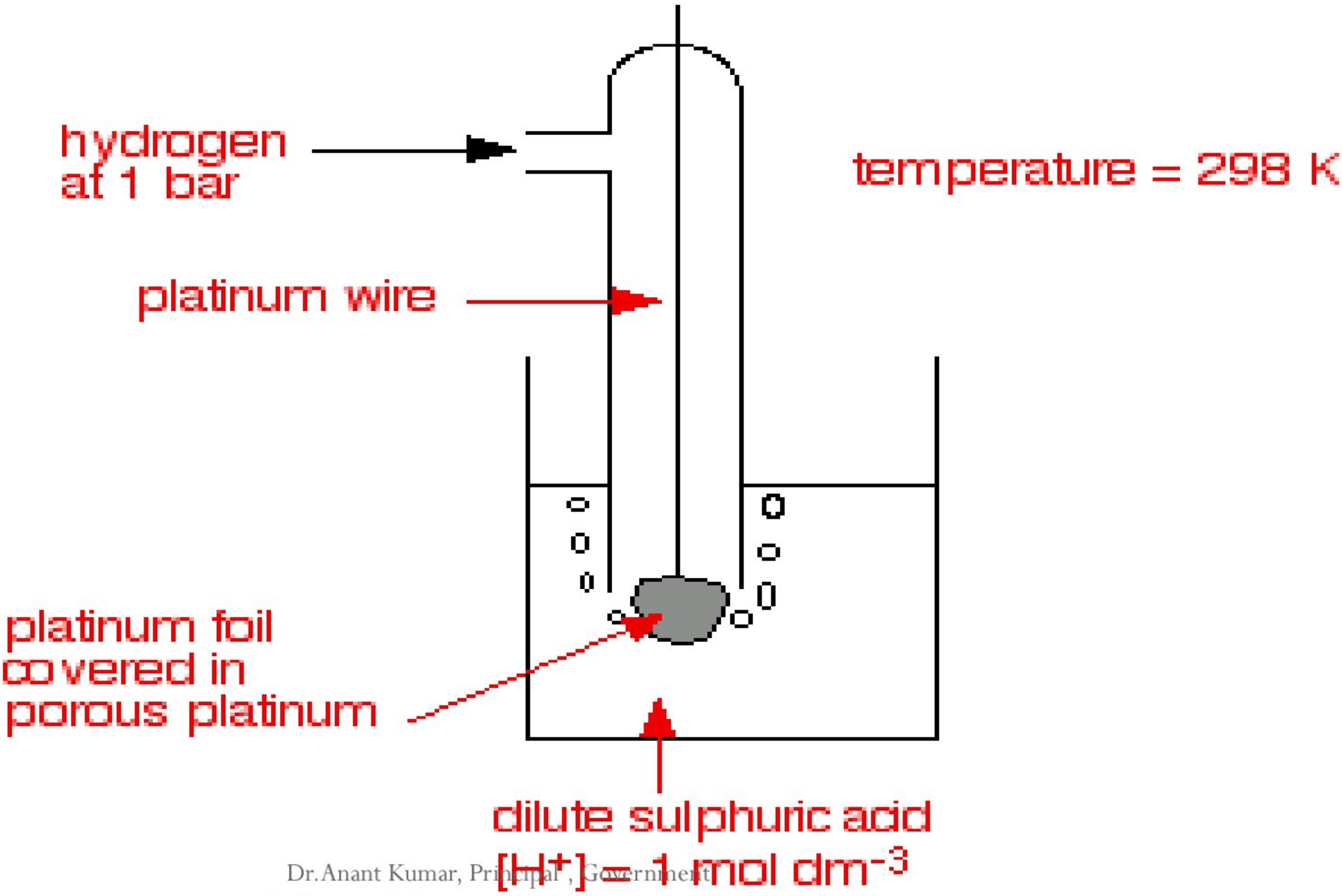
$E^0$ = with saturated KCl solution is 0.2422 V and for 0.1N KCl is 0. 335V at $25^0C$ with reference to SHE

- **Silver-Silver Chloride electrode**

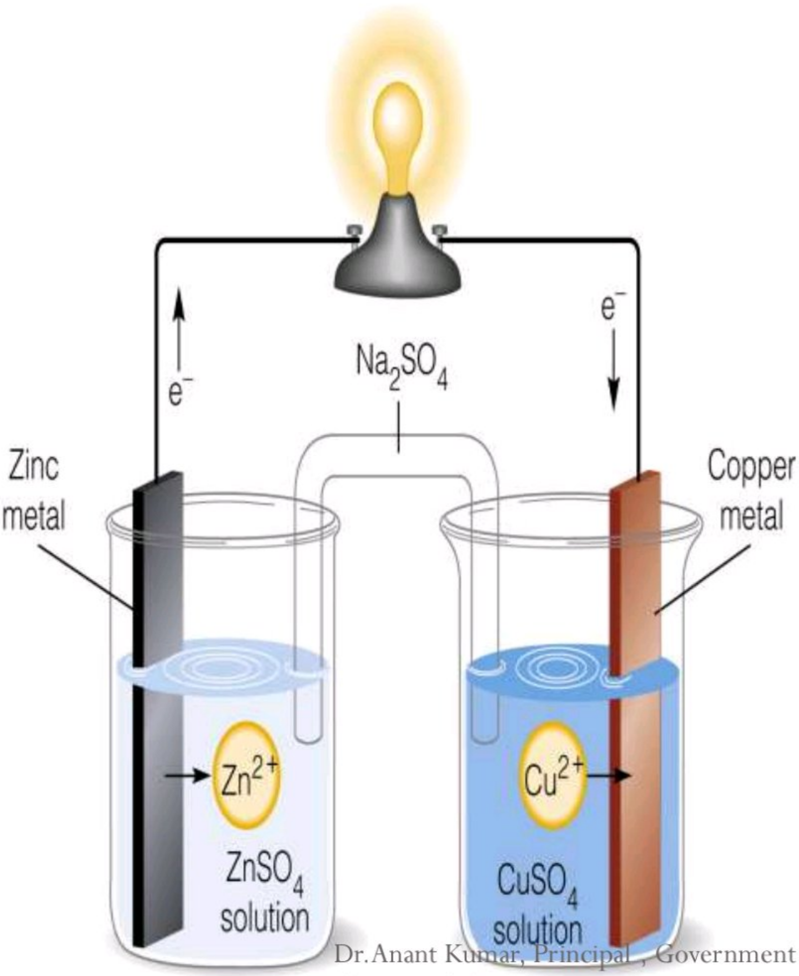
  Ag |AgCl, $Cl^-$

  $E^0$ = with saturated KCl solution is 0.29 V and for 0.1N KCl is 0. 199V at $25^0C$ with reference to SHE

# STANDARD HYDROGEN ELECTRODE



## GALVANIC CELL




- **Anode:** Where oxidation takes place , e. g Zn-rod. Zn loses electron, it becomes the source of electron so it acquires –ve charge.
- **Cathode:** Where reduction takes place , e. g Cu-rod. $Cu^{+2}$ accepts electron, it becomes the sink of electron so it is termed as +vely charged.
- **Function of Porous plate or Salt Bridge:** To maintain the electrical neutrality. In salt bridge that salt is used for which the should be same.

## REPRESENTATION OF DANIEL CELL

- Oxidation at L.H.S. & Reduction at R.H.S.
- Small vertical bar between oxidized & Reduced state.
- Two vertical Parallel bars between Oxidation and Reduction process e.g. $Zn(s) | Zn^{+2}(aq) || Cu^{+2}(aq) | Cu(s)$
- If Inert electrode, like Pt, is used , it must be placed at extremely L.H.S in oxidation process at R.H.S. in case of Reduction as**:**

  **$Pt, H_2\,(1atm) \;|\; HCl_{(1M)} \;||\; Fe^{+3}, Fe^{+2}, Pt$**
- Electrode of a metal , its sparingly soluble salt and solution of a soluble salt of the same anion can be represented as :

  Ag , AgCl (s) HCl

  The reaction occurs as : $Ag\,(s) = Ag^{+} + e$ .

  $Ag^{+}$ interacts with $Cl^{-}$

  $Ag^{+} + Cl^{-} = AgCl\,(s)$ . The net reaction is : $Ag(s) + Cl^{-} = AgCl_{(s)}$

## CALCULATION OF $E^0$

- $E^o$ for complete reaction may be added as (**$E_{ox}^o$ + $E_{red}^o$** ) no electrons are left over in the process:
- **Q.7.** Calculate the for $Mg_{(s)} + Cu^{+2}(aq) = Mg^{+2} + Cu_{(s)}$ $E^o$ for $Mg^{+2}$ / $Mg_{(s)}$ & $Cu^{+2}$ /Cu are –2.360 & 0.347V?

  Which one is oxidizing & reducing agent between Cu & Mg?

  (Ans: 2.697V)

- Potential does not depend on the quantity.

**Q.8.** Calculate $E^o$ for cell ; Zn | $Zn^{+2}$(1M) || $Fe^{+2}$(1M) | $Fe^{+3}$(1M), Pt.

$E^o$ for $Fe^{+3}$ / $Fe^{+2}$ & $Zn^{+2}$ /Zn are 0.77 & -0.76V respectively.

(Ans: 1.53V)

- $E^o$ may not be added for half reaction since the electrons may not balance. However $E^o$ can always be converted into $\Delta G^o$ using equation $\Delta G^o = -nFE^o$. G is a thermodynamic function so it may be added and finally converted back to an $E^o$ value.

**Q.9.** Calculate $E^o$ for $Fe^{+3} + 3e = Fe$? $E^o$ for $Fe^{+3}$ / $Fe^{+2}$ & $Fe^{+2}$/ Fe 0.77V & -0.47V are respectively. (Ans:-0.057V)

## RELATION BETWEEN 'E' AND '$E^0$'

➢ NERNST Equation establishes relation **'E' and '$E^0$'**

$$E = E^o - \frac{2.303RT}{nF} \log Q$$

where Q is reaction quotient.

At $25^0$c ; $\frac{2.303RT}{F} = 0.0591$ ; $\mathbf{E = E^o - \frac{0.0591}{n} \log Q}$

- **<u>Applications of Nernst equation.</u>**

**(a) To calculate E at any concentration.**

**Q. 10.** Calculate $E_{cell}$ for $Mg_{(s)} + Cu^{+2}(aq) = Mg^{+2} + Cu_{(s)}$ $E^o$ for $Mg^{+2}/Mg_{(s)}$ & $Cu^{+2}/Cu$ are –2.360 & 0.337v and concentration $[Mg^{+2}] = 0.001M$ & $[Cu^{+2}] = 0.0001M$? (Ans: 2.73V)

**(b) To calculate the pH of solution:**

Q.11. A galvanic cell consisting of a Cu vs Hydrogen electrode was used to determine the pH of an unknown solution. The unknown solution was placed in the Hydrogen electrode compartment under the pressure of the $H_2$ gas controlled at 1atm. $[Cu^{+2}]$ was 1M and $E_{cell} = 0.48V$. Calculate the pH of solution?(Ans: 2.4)

**(c) To calculate the Electrode potential for half cell reaction at any concentration:**

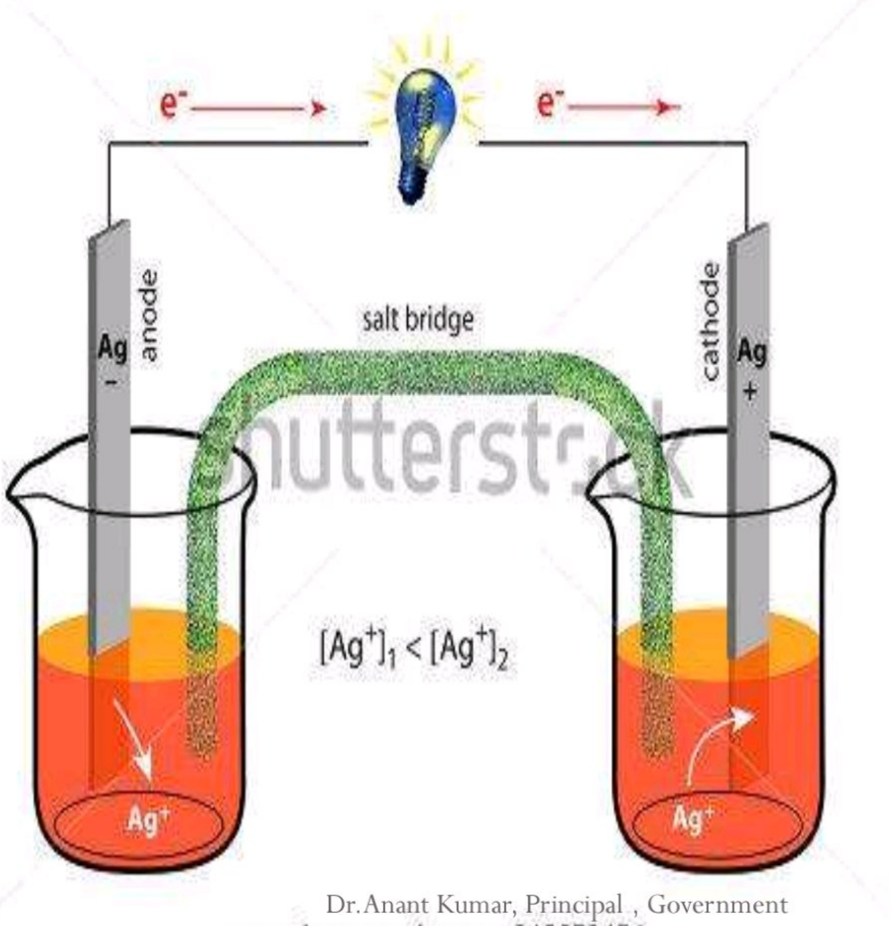
Half cell reaction should be expressed in terms of reduction.

Q.12. Calculate $E_{cu^{+2}/Cu}$ if the $[Cu^{+2}] = .01M$?

**(d) To find Solubility & solubility product.**

**Q.13** For a cell reaction $Pb(s) + Sn^{+2}(1M) = Pb^{+2}(aq) + Sn(s)$. Find the Ksp of $PbSO_4$? $E^o$ for $Sn^{+2} / Sn_{(s)}$ & $Pb^{+2}/Pb$ are –0.14 & -0.13V. $[SO_4] = 1M$, $E_{cell} = 0.22V$

# CONCENTRATION CELL




- Energy released, during transfer of mass from higher to lower concentration, is converted into electrical energy.
- Oxidation occurs at lower concentration & reduction at higher concentration.
- NERNST Equation

$$E = 0.0591 \log \frac{[Ag^+]_2}{[Ag^+]_1}$$

**Q.14**. Calculate the emf at $25^0$c, of the concentration cell

$Ag_{(s)}$ | $AgNO_3$(0.01M) || $AgNO_3$(1M) | $Ag_{(s)}$ (Ans: 0.12V)

**Q.15.** Find Keq for rev. reaction:

riboflavin (ox) + rubredoxin (red) = riboflavin (red) + rubredoxin (ox)

Given that; pH= 7; Standard Electrode Potential for riboflavin and rubredoxin is -0.21 and -0.06V respectively. (Ans: $8.42 \times 10^{-6}$)

**Q.16.** Find Keq for rev. reaction;

RibO(aq) + $CH_3CHO$(aq) = Rib (aq) + $CH_3COOH$(aq)

$E^0_{RibO|Rib}$ ; $E^0_{CH3CHO|CH3COOH}$ is -0.21 and +0.60V respectively. (Ans: $1.56 \times 10^{23}$)

**Q.17.** Find $\Delta G$, $\Delta H$ and $\Delta S$ of the cell reaction for standard Cd-Cell?

Given; E= 1.02V; $\{\Delta E/ \Delta T\}_P$ = -5 x 10-5 V $k^{-1}$

(Ans: $\Delta G$ =$-1.97 \times 10^5$; $\Delta H$ =$1.99 \times 10^5$J $mol^{-1}$ $VK^{-1}$;

$\Delta S$=-9.65 J $K^{-1}$ $mol^{-1}$)

# BATTERIES

- **Primary Batteries:** Reaction occurs only once and becomes dead. It can not be reused e.g.

    - Le-Clanche Cell,
    - Dry Cell

- **Secondary Cell:** Rechargeable by passing a current through it in opposite direction so that it can be used again e.g.

    - Lead storage Battery
    - Nickel – Cadmium Cell

## DIFFERENCES

| Primary Batteries | Secondary Batteries |
|---|---|
| Cell reaction is irreversible | Cell reaction is reversible. |
| Must be discarded after use. | May be recharged |
| Have relatively short shelf life | Have long shelf life. |
| Function only as galvanic cells . | Functions both galvanic Cell & as electrolytic cell. |
| They cannot be used as storage devices | They can be used as energy storage devices (e.g. solar/ thermal energy converted to electrical energy) |
| They cannot be recharged e.g. Dry cell. | They can be recharged. $Li\text{-}MnO_2$ battery. Lead acid, Ni-Cd battery. |

# PRIMARY BATTERIES

## Le-Clanche Cell

- **Anode** : Zn container
- **Cathode** : Graphite rod surrounded by Powder $MnO_2$ & C
- **Electrolyte** :

  Moist paste of $\mathbf{NH_4Cl}$ **&** $\mathbf{ZnCl_2}$
- **Cell Reaction:**

  $Zn(s) \rightarrow Zn^{+2} + 2e$ (anode)

  $MnO_2 + NH_4^{+} + e \rightarrow Mn(OH) + NH_3$ (Cathode)
- $NH_3$ is not liberated at cathode because $Zn^{+2}$ form complex $[Zn(NH_3)_4]^{+2}$. Dry cells do not have infinite life because acidic corrodes the Zn-container even when it is not in use. Dry cells have potential of approx 1.25 to 1.5V.

## Dry Cell

- **Anode** : Zn-Hg
- **Cathode** : Paste of HgO + C
- **Electrolyte** : Paste of KOH & ZnO
- **Cell Reaction :**

  $Zn(Hg) + 2OH^- \rightarrow ZnO(s) + H_2O + 2e$ (anode)

  $HgO_{(s)} + H_2O + 2e \rightarrow Hg(l) + 2OH^-$ (cathode)

  $Zn(Hg) + HgO_{(s)} \rightarrow ZnO_{(s)} + Hg_{(l)}$
- Since the overall reaction does not involve any ion in solution whose concentration can change, the cell shows constancy in potential through out its life. The cell potential is approx. 1.35V.
- Used in small electrical circuit such as hearing aids ,watches & camera

# BASIC REQUIREMENTS OF PRIMARY CELL.

- Compactness and lightweight.
- Fabricated from easily available raw materials.
- Economically priced.
- High energy density and constant voltage.
- Benign environmental properties
- Longer shelf life and discharge period.
- Leak proof containers and variety of design options.

## BASIC REQUIREMENTS OF SECONDARY CELL.

- Long shelf-life and cycle life.
- High power to weight ratio
- Short time for recharging
- Tolerance to service condition.
- High voltage & high energy density.

## SECONDARY CELL

### (i) Lead storage Battery

- Anode : Lead
- Cathode : Grid of Lead-Antimony alloy packed with Lead Oxide
- Electrolyte : 20% solution of $H_2SO_4$ (sp.gravity=1.5 at $25^0$c)
- Charging Cell Reaction:

$PbSO_4(s) + 2e \rightarrow Pb(s) + SO_4^{-2}$ (Cathode)

$PbSO_4(s) + 2H_2O \rightarrow PbO_2(s) + SO_4^{-2}(aq) + 2H^+(aq) + 2e$ (Anode)

- Net Reaction

$PbSO_4(s) + 2H_2O + Energy \rightarrow Pb(s) + PbO_2 + 4H^+ + 2SO_4^{-2}$

- On charging the battery the reaction is reversed and $PbSO_4(s)$ on anode and cathode is converted into Pb & $PbO_2$ respectively.

## DISCHARGING CELL REACTION

$Pb(s) \longrightarrow Pb^{+2}(s) + 2e$ (Anode)

$Pb^{+2}$ combines with $SO_4^{-2}$

$Pb^{+2} + SO_4^{-2}(aq) \longrightarrow PbSO_4(s)$

$PbO_2(s) + 2H^+ + 2e \longrightarrow Pb^{+2} + 2H_2O$ (Cathode)

$Pb^{+2}$ combines with $SO_4^{-2}$

The net reaction is:

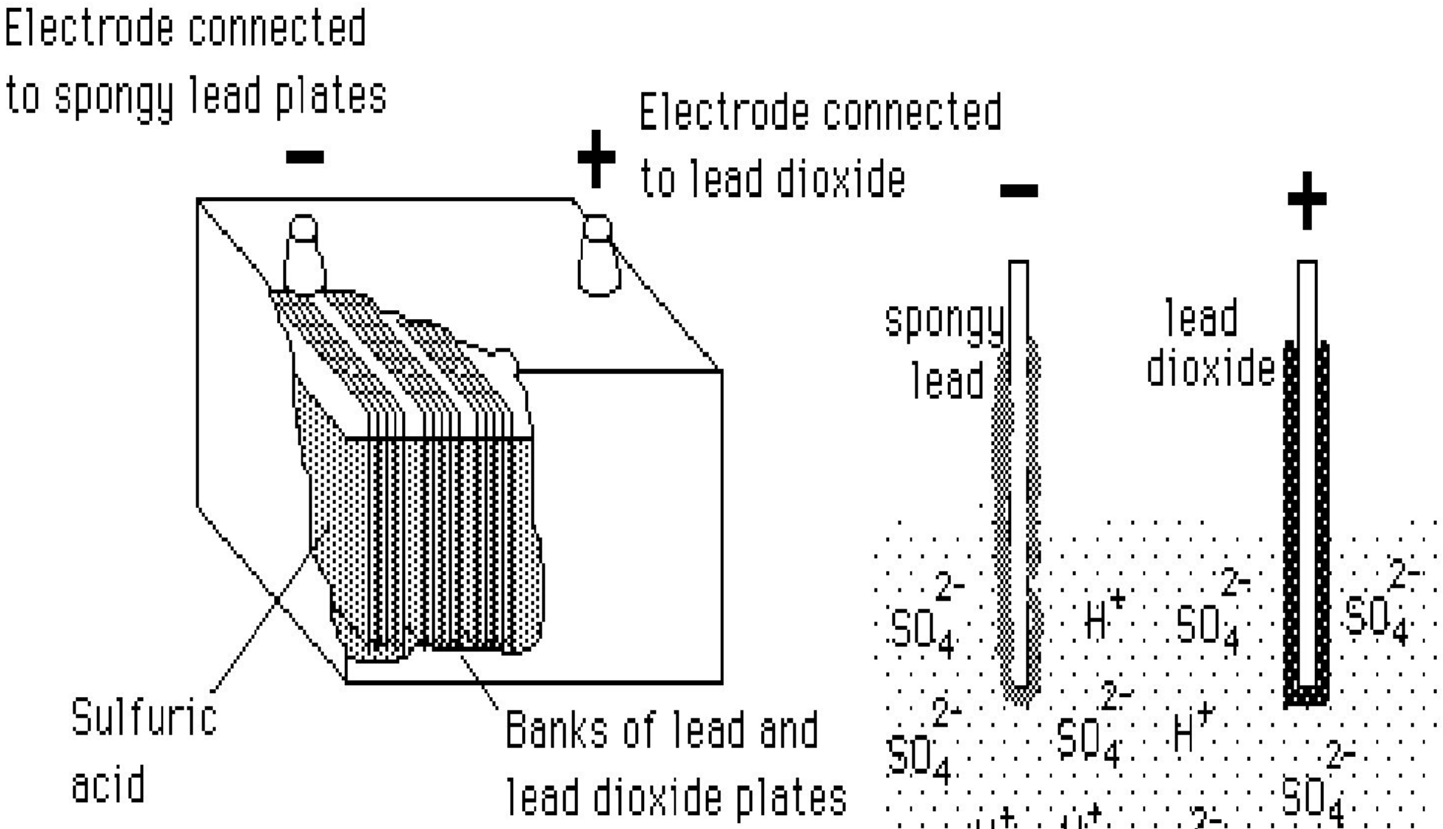
$$Pb + PbO_2 + 4H^+ + 2SO_4^{-2}(aq) \longrightarrow 2PbSO_4(s) + 2H_2O\ (l) + E$$

- The voltage of each cell is about 2.0V at a concentration of 21.4%. So, six lead-acid storage cells in a car gives 12 volts.

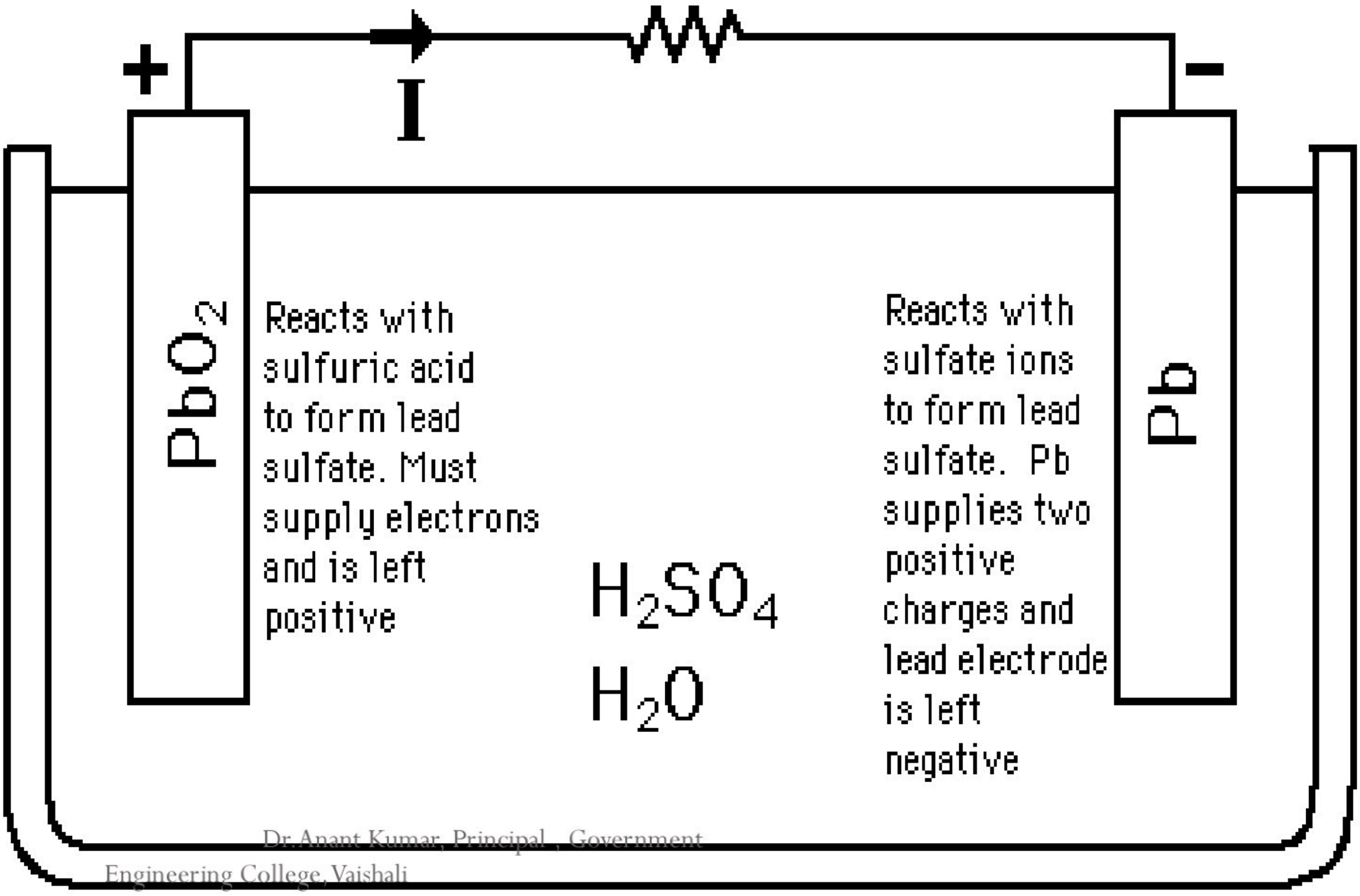
## (ii) NICKEL – CADMIUM CELL

- **Anode** **:**Cd
- **Cathode** **:**Ni
- **Electrolyte** **:**Sodium or Potassium hydroxide
- **Cell Reaction:**
  $Cd(s) + 2Ni(OH)_3(s) \rightarrow$
  $CdO\ (s) + 2Ni(OH)_2\ (s) + 2H_2O\ (l)$
- It has longer life than Lead storage Battery.

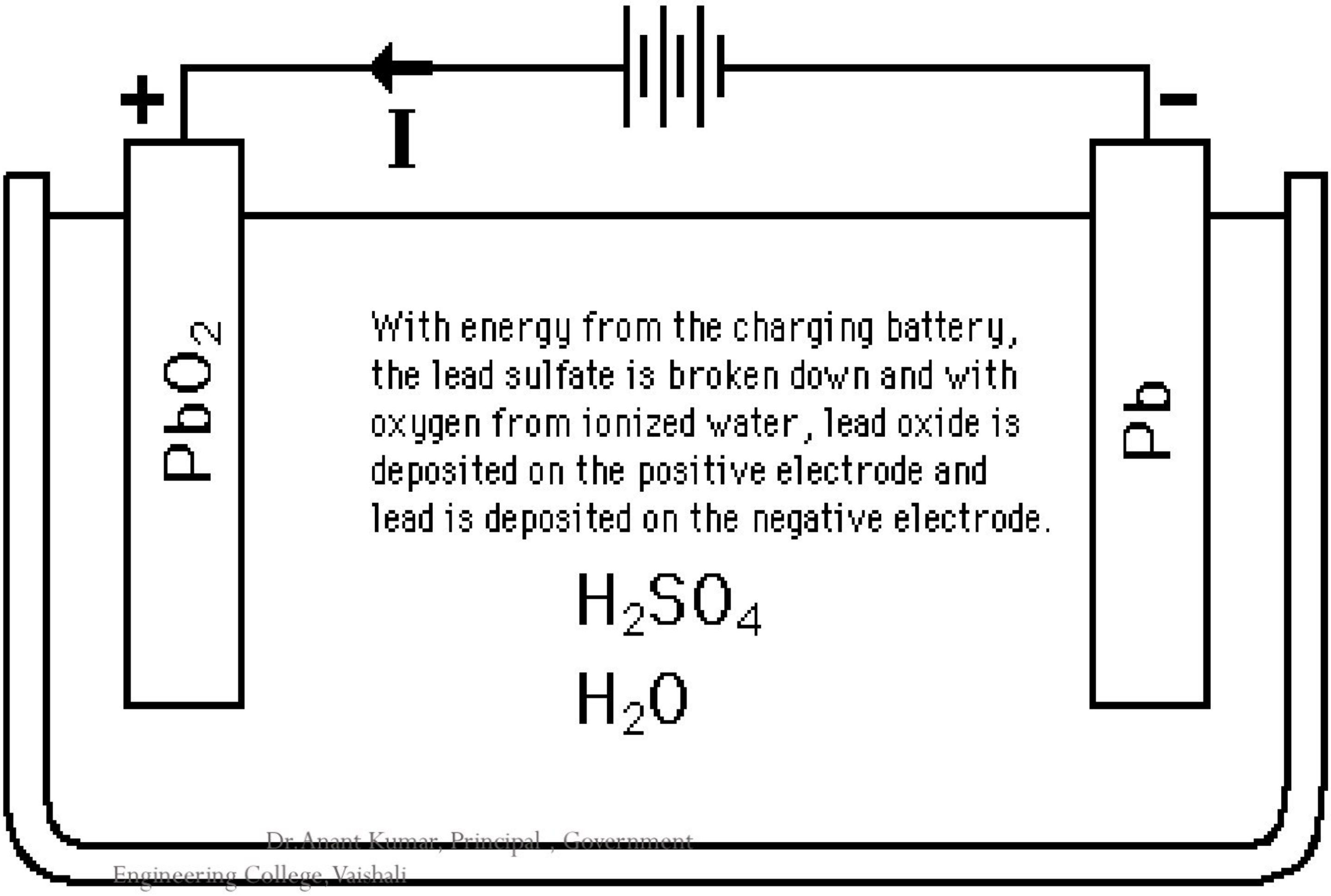
# LEAD-ACID BATTERY:



# LEAD STORAGE BATTERY.



# CHARGING THE LEAD-ACID BATTERY:



## LIMITATIONS.

- Self discharge: They are subject to self discharge with $H_2$ evolution at negative plates and $O_2$ evolution at positive plates.

$$Pb + H_2SO_4 \rightarrow PbSO_4 + H_2$$
$$PbO_2 + H_2SO_4 \rightarrow PbSO_4 + H_2O + 1/2\, O_2$$

$$SO_4^{2-} + 2\,H^+ \text{ (From dissociation of water)} \rightarrow H_2SO_4$$
$$H_2O \rightarrow H^+ + OH^-$$

- Loss of Water: Due to evaporation, self discharge and electrolysis of water while charging. *Hence water content must be regularly checked and distilled water must be added.*

- Sulfation: If left in uncharged state, for a prolonged period, or operated at too high temperatures or at too high acid concentrations, transformation of porous $PbSO_4$ into dense and coarse grained form by re crystallization.

  * *This results in passivation of negative plates inhibiting their charge acceptance.*

- Corrosion of Grid: Can occur due to overcharging when grid metal gets exposed to the electrolyte. *This weakens the grid and increases the internal resistance of the battery.*

- Effectiveness of battery is reduced at low temperature due to increase in the viscosity of electrolyte

- Recent years have seen the introduction of "maintenance – free batteries" without a gas – release vent. Here the gassing is controlled by careful choice of the composition of the lead alloys used i.e. by using a Pb-Ca (0.1 % ) as the anode which inhibits the electrolysis of water.

- Alternatively, some modern batteries contain a catalyst (e.g. a mixture of 98% ceria (cerium oxide) & 2% platinum, heated to $1000^{o}$ C) that combines the hydrogen and oxygen produced during discharge back into water. Thus the battery retains its potency and requires no maintenance. Such batteries are sealed as there is no need to add water and this sealing prevents leakage of cell materials.

## APPLICATIONS.

Automative: For starting, lighting and ignition of IC engine driven vehicles.

*Consumer Applications: Emergency lighting, security alarm system.

*Heavy duty Application: Trains, lift trucks, mining machines etc.

## Advantages:

A lead storage battery is highly efficient. The voltage efficiency of the cell is defined as follows.

$$\text{Voltage efficiency} = \frac{\text{average voltage during discharge}}{\text{average voltage during charge}}$$

The voltage efficiency of the lead – acid cell is about 80 %.

The near reversibility is a consequence of the faster rate of the chemical reactions in the cell i.e. anode oxidizes easily and cathode reduces easily leading to an overall reaction with *a high negative free energy change.*

- A lead – acid battery provides a good service for several years. Its larger versions can last 20 to 30 years, if carefully attended (i.e. longer design life)

- It can be recharged. The number of recharges possible range from 300 to 1500, depending on the battery's design and conditions. The sealed lead-acid batteries can withstand up to 2000 – recharging. Generally the most costly, largest, heaviest cells are the longest–lived.

- The battery's own internal self – discharging is low.

- The length of time that is generally required for re-charging process is less i.e. recharge time is 2-8 hours depending on the status of battery.

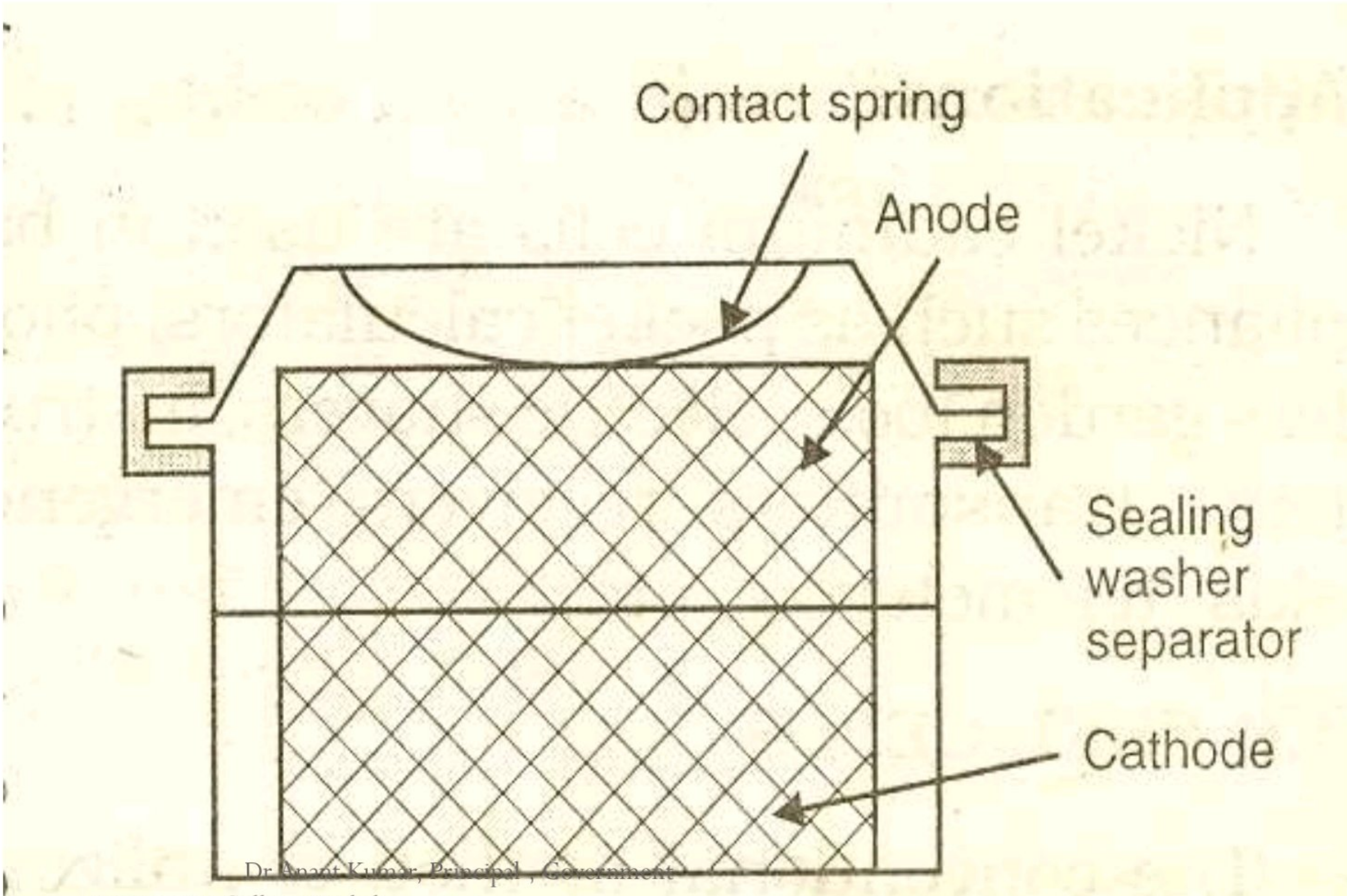
- Low environmental impact of constituent materials is an added advantage

- It has sensitivity to rough handling and good safety characteristics.

- Ease of servicing as indicated by several local battery service points.

- It is a low- cost battery with facilities for manufacture throughout the world using cheap materials.

## NICKEL- CADMIUM CELL



## REACTIONS

Anode : Porous cadmium powder compressed to cylindrical pellets.

Cathode: $Ni(OH)_3$ or $NiO(OH)$ mixed with 20% graphite powder

Electrolyte: 20-28% Aq. KOH jelled with a jelling agent.

*Cell Scheme:* $Cd/Cd(OH)_2, KOH, Ni(OH)_2, Ni(OH)_3/Ni$

O.C.V. = 1.25V

# REACTIONS DURING DISCHARGING

Anode:

$Cd_{(s)} + 2OH^{-}_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2e^{-}$

Cathode:

$2Ni(OH)_{3(s)} + 2e^{-} \rightarrow 2Ni(OH)_{2(s)} + 2OH^{-}_{(aq)}$

- Net Reaction:

*$Cd_{(s)} + 2Ni(OH)_{3(s)} \rightarrow 2Ni(OH)_{2(s)} + Cd(OH)_{2(s}$*

# CHARGING REACTIONS:

**Anode:**

$Cd(OH)_{2(s)} + 2e^- \rightarrow Cd_{(s)} + 2OH^-_{(aq)}$

Cathode:

$2Ni(OH)_{2(s)} + 2OH^-_{(aq)} \rightarrow 2Ni(OH)_{3(s)} + 2e^-$

Net:

$2Ni(OH)_{2(s)} + Cd(OH)_{2(s)} \rightarrow 2Ni(OH)_{3(s)} + Cd_{(s)}$

## DISCHARGING REACTION:

- Anode: $Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$
- *Cathode*: $2NiO(OH)(s) + 2H_2O + 2e^- \rightarrow$
  $2Ni(OH)_2(s) + 2OH^-(aq)$
- Net Reaction:

$$Cd(s) + 2NiO(OH)(s) + 2H_2O \rightarrow 2Ni(OH)_2(s) + Cd(OH)_2(s)$$

# CHARGING REACTIONS:

- -ve pole: $Cd(OH)_2\ (s) + 2e^- \rightarrow Cd(s) + 2OH^-(aq)$
- +ve pole: $2\ Ni(OH)_2(s) + 2OH^-(aq) \rightarrow 2\ NiO(OH)\ (s) + 2H_2O + 2e^-$
- Overall reaction: $2\ Ni(OH)_2\ (s) + Cd(OH)_2(s) \rightarrow 2\ NiO(OH)\ (s) + Cd(s) + 2H_2O(l)$

## APPLICATIONS.

- *In flash lights, photoflash units and portable electronic equipments.*

- *In emergency lighting systems, alarm systems.*

- *In air crafts and space satellite power systems.*

- *For starting large diesel engines and gas turbines etc.,*

## ADVANTAGES.

- *Can be recharged many times.*
- *They maintain nearly constant voltage level throught their discharge. There is no change in the electrolyte composition during the operation.*
- *It can be left unused for long periods of time at any state of charge without any appreciable damage (i.e. long shelf life).*
- *It can be encased as a sealed unit like the dry cell because gassing will not occur during nominal discharging or recharging.*
- *They exhibit good performance ability at low temperatures.*

- *They can be used to produce large instantaneous currents as high as 1000-8000 A for one second.*

- *It is a compact rechargeable cell available in three basic configurations – button, cylindrical and rectangular.*

- *They have low internal resistance.*

## DISADVANTAGES.

- *It poses an environmental pollution hazard due to higher toxicity of metallic cadmium than lead.*

- *Cadmium is a heavy metal and its use increases the weight of batteries, particularly in larger versions.*

- *Cost of cadmium metal and hence the cost of construction of NiCad batteries is high.*

- *The KOH electrolyte used is a corrosive hazardous chemical.*

# FUEL CELLS.

A fuel cell is a galvanic cell in which chemical energy of a fuel – oxidant system is converted directly into electrical energy in a continuous electrochemical process.

- Cell Schematic Representation:

  Fuel;electrode/electrolyte/electrode/oxidant.

  e.g. $H_2$-$O_2$;     $CH_3OH$-$O_2$

- The reactants (i.e. fuel + oxidant) are constantly supplied from outside and the products are removed at the same rate as they are formed.
- Anode:

  Fuel+ oxygen → Oxidation products+ $ne^-$
- Cathode:

  Oxidant + $ne^-$ → Reduction products.

## REQUIREMENTS OF FUEL CELL.

- Electrodes: Must be stable, porous and good conductor.
- Catalyst: Porous electrode must be impregnated with catalyst like Pt, Pd, Ag or Ni, to enhance otherwise slow electrochemical reactions.
- Optimum Temperature: Optimum.
- Electrolyte: Fairly concentrated.

## HYDROGEN – OXYGEN FUEL CELL

- Anode: Porous graphite electrodes impregnated with finely divided Pt/Pd.
- Cathode: Porous graphite electrodes impregnated with finely divided Pt/Pd.
- Electrolyte: 35-50% KOH held in asbestos matrix.
- Operating Temperature: $90^{o}C$.

- Anode :

$$2H_{2(g)} + 40H^{-}_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^{-}$$

- Cathode:

$$O_{2(g)} + 2H_2O_{(l)} + 4e^{-} \rightarrow 4OH_{(aq)}$$

- Net Reaction:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}.$$

*Water should be removed from the cell.

*$O_2$should be free from impurities.

## APPLICATIONS

- Used as energy source in space shuttles e.g. Apollo spacecraft.
- Used in small- scale applications in submarines and other military vehicles.
- Suitable in places where, environmental pollution and noise are objectionable.

## $CH_3OH$-$O_2$ Fuel cell

- Both electrodes: Made of porous nickel plates impregnated with finely- divided Platinum.
- Fuel: Methyl alcohol.
- Oxidant: Pure oxygen / air.
- Electrolyte: Conc.Phosphoric acid/Aq.KOH
- Operating Temperature: 150-200$^{o}$C.

- The emf of the cell is 1.20V at 25°C.
- MeOH is one of the most electro active organic fuels in the low temperature range as

  *It has a low carbon content

  *It posseses a readily oxidizable OH group

  *It is miscible in all proportions in aqueous electrolytes.

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  *It is miscible in all proportions in aqueous electrolytes.

- At anode:

$$CH_3OH + 6OH^- \rightarrow CO_2 + 5H_2O + 6e^-$$

- At cathode:

$$3/2\ O_2 + 3H_2O + 6e^- \rightarrow 6OH^-$$

***Net Reaction:***

$$\boldsymbol{CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O.}$$

***It is used in millitary applications and in large scale power production. It has been used to power television relay stations.***

## LIMITATIONS OF FUEL CELLS.

- Cost of power is high as a result of the cost of electrodes.
- Fuels in the form of gases and $O_2$ need to be stored in tanks under high pressure.
- Power output is moderate.
- They are sensitive to fuel contaminants such as $CO$,$H_2S$, $NH_3$ & halides, depending on the type of fuel cell.

## ADVANTAGES OF FUEL CELLS.

- High efficiency of the energy conversion process.
- Silent operation.
- No moving parts and so elimination of wear and tear.
- Absence of harmful waste products.
- No need of charging.

- *They can be used to produce large instantaneous currents as high as 1000-8000 A for one second.*
- *It is a compact rechargeable cell available in three basic configurations – button, cylindrical and rectangular.*
- *They have low internal resistance*

## DIFFERENCES.

| Fuel Cell | Galvanic Cell |
|---|---|
| *Do not store chemical energy | Stores chemical energy |
| *Reactants are fed from outside continuously. | The reactants form an integral part of it. |
| *Need expensive noble metal catalysts. | These conditions are not required |
| *No need of charging | Get-discharged when stored – up energy is exhausted. |
| *Never become dead | Limited life span in use |
| *Useful for long-term electricity generation. | Useful as portable power services |

## CORROSION

- **Principle:** When oxygen of the air is in contact with a moist metal surface , the corrosion is promoted. Certain part of the moist metal are less oxygenated . This forms a concentration Cell. Anode becomes less oxygenate part & cathode more Oxygenated part. Reaction takes place as :
- $Fe(s) \rightarrow Fe^{+2} + 2e$ (Anode)
- $O_2 + 4H^+ + 4e \rightarrow 2H_2O\ (l)$ (Cathode)
- $Fe(s) + O_2 + 4H^+ \rightarrow 2Fe^{+2} + H_2O(l)$
- $Fe^{+2}$ is further oxidized to $Fe^{+3}$ by atmospheric Oxygen which comes out as rust in the form of hydrated Iron Oxide ; $Fe_2O_3.xH_2O$.

- **Factors which enhance Corrosion:**

  (i) $[H^+]$

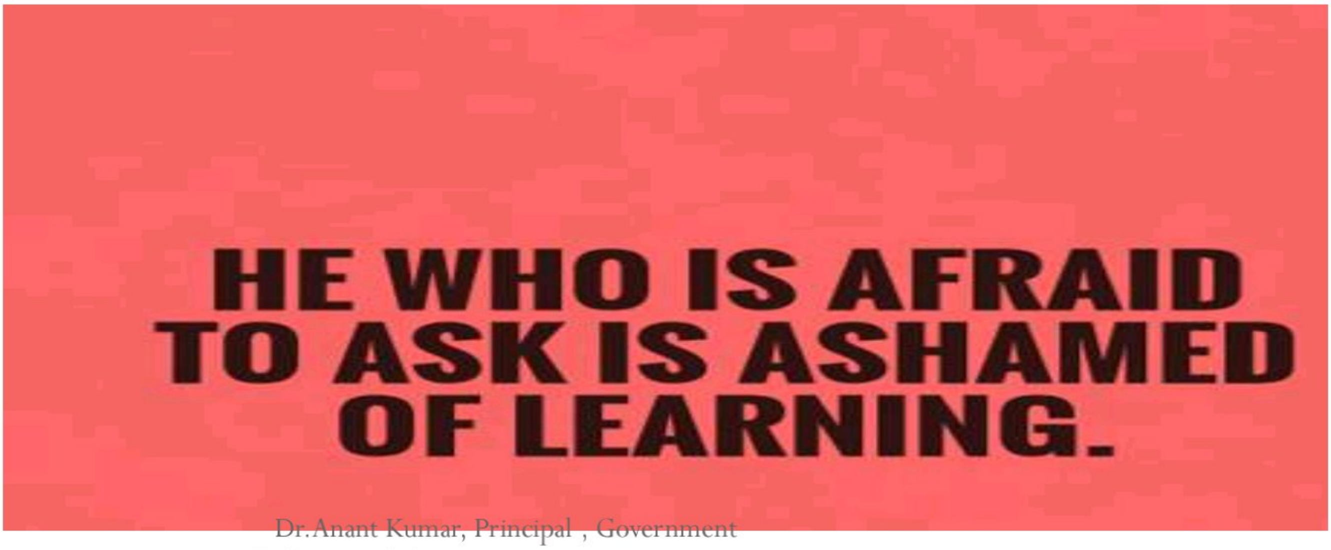
  (ii) Salinity of water.

- **Protection:**

(i) By electroplating

(ii) Applying Paint.


TIME FOR QUESTIONS


HE WHO IS AFRAID
TO ASK IS ASHAMED
OF LEARNING.


Dr.Anant Kumar, Principal , Government Engineering College, Vaishali