



Electrochemistry

UNIT III

**Subject: Chemistry II Subject Code :
KAS202**

Class: B.Tech. I SEM: II

Branch : CSE, IT, ME, EE, ECE & EIE

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- ❖ Nernst Equation and its Application
- ❖ Relation of EMF with Thermodynamic Function
- ❖ Lead Storage Battery
- ❖ Corrosion, Cause, Effect & Prevention

Course Contents

The **Nernst Equation** enables the determination of **cell potential** under **non-standard conditions**. It relates the measured cell potential to the reaction quotient and allows the accurate determination of equilibrium constants.
The **Nernst Equation** is derived from the **Gibbs free energy** under **standard conditions**.

$$E^0 = E^0_{\text{reduction}} - E^0_{\text{oxidation}} \quad [1]$$

The maximum work done is :

$$W_{\text{max}} = -nFE$$

But according to thermodynamics the change in Gibbs Free Energy in Std. & non-Std. Condition will be:

$$\Delta G = -nFE \text{ (non-Standard Condition)} \quad [2]$$

and

$$\Delta G = -nFE^0 \text{ (Standard condition)} \quad [3]$$

Where

- $\Delta G \rightarrow$ Gibbs Free Energy
- $\Delta G^0 \rightarrow$ Standard Gibbs Free Energy
- $n \rightarrow$ no of Electrons
- $E^0 \text{ \& } E \rightarrow$ Cell Electrode Potential
- $F \rightarrow$ Faraday Constant (96,500 C/mol)



Walther H. Nernst
(1864-1941)

Received the Nobel prize in
1920

As we know when :

$E^0 \rightarrow$ +ve reaction is spontaneous

$E^0 \rightarrow$ -ve reaction is not spontaneous

$E^0 = 0$ reaction at Equilibrium

From **thermodynamics**, the **Gibbs energy change** under **non-standard conditions** can be related to the **Gibbs energy change** under standard Equations *via*

$$\Delta G = \Delta G^0 + RT \ln Q \quad [4]$$

Substituting the value of $\Delta G = -nFE$ and $\Delta G^0 = -nFE^0$ in equation [4], we have:

$$-nFE = -nFE^0 + RT \ln Q \quad [5]$$

Divide both side of equation [5] by $-nF$, we have

$$E = E^0 - \frac{RT}{nF} \ln Q \quad [6]$$

The equation [6] can be rewritten in form of \log_{10} { $\ln = 2.303 \log$ and $\log \frac{A}{B} = -\frac{B}{A}$ }



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$$E = E^0 - \frac{2.303RT}{nF} \log_{10} Q \quad [7]$$

At standard temperature $T = 298 \text{ K}$, the $\frac{2.303RT}{F}$ term equal to 0.0591V and Equation [7] can be rewritten:

$$E = E^0 - \frac{0.0592\text{V}}{n} \log_{10} Q \quad [8]$$

The Equation above indicate that the electrical potential **[E]** of a cell depends upon the reaction quotient **Q** of the reaction. As the **redox reaction** proceeds, **reactants are consumed**, and thus **concentration of reactants decreases**. Conversely, the **products concentration** increases due to the increased in products formation.

As this happens, cell potential **[E]** gradually decreases until the reaction is at **Equilibrium** at which $\Delta G = 0$. At the Equilibrium, the reaction Quotient $Q = K_{eq}$.

Also, at Equilibrium $\Delta G = 0$ and $\Delta G = -nFE$, so $E = 0$

Therefore, substituting $Q = K_{eq}$ and $E = 0$, into Nernst Equation [8], we have

$$0 = E^0 - \frac{RT}{nF} \ln K_{eq} \quad [9]$$



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At room temperature, Equation [9] simplifies into (notice natural log was converted to log base₁₀):

$$0 = E^{\circ} - \frac{0.0592V}{n} \log_{10} K_{eq} \quad [10]$$

This can be rearranged to:

$$\log K_{eq} = \frac{nE^{\circ}}{0.0592V} \quad [11]$$

The Equation above indicates that the equilibrium constant K_{eq} is proportional to the **standard potential $[E^{\circ}]$** of the reaction. Specifically, when:

$K > 1, E^{\circ} > 0$, reaction favors products formation.
 $K < 1, E^{\circ} < 0$, reaction favors reactants formation.

This result fits **Le Châtlier's Principle**, which states that when a system at equilibrium experiences a change, the system will minimize that change by shifting the equilibrium in the opposite direction



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The reaction Quotient (Q) is :

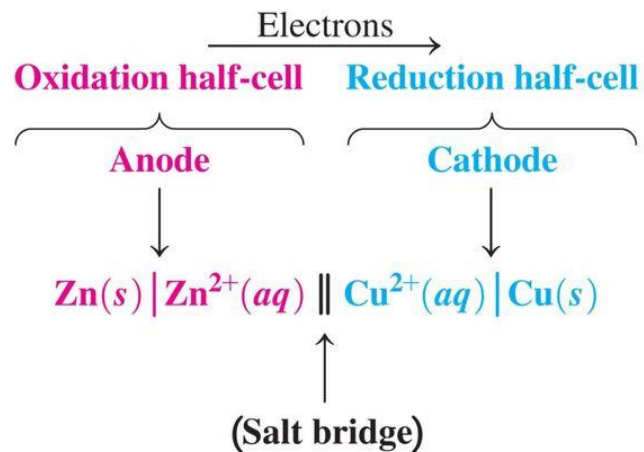
$$Q = \frac{[\text{Product}]}{[\text{Reactan}]}$$

In Electrochemistry :

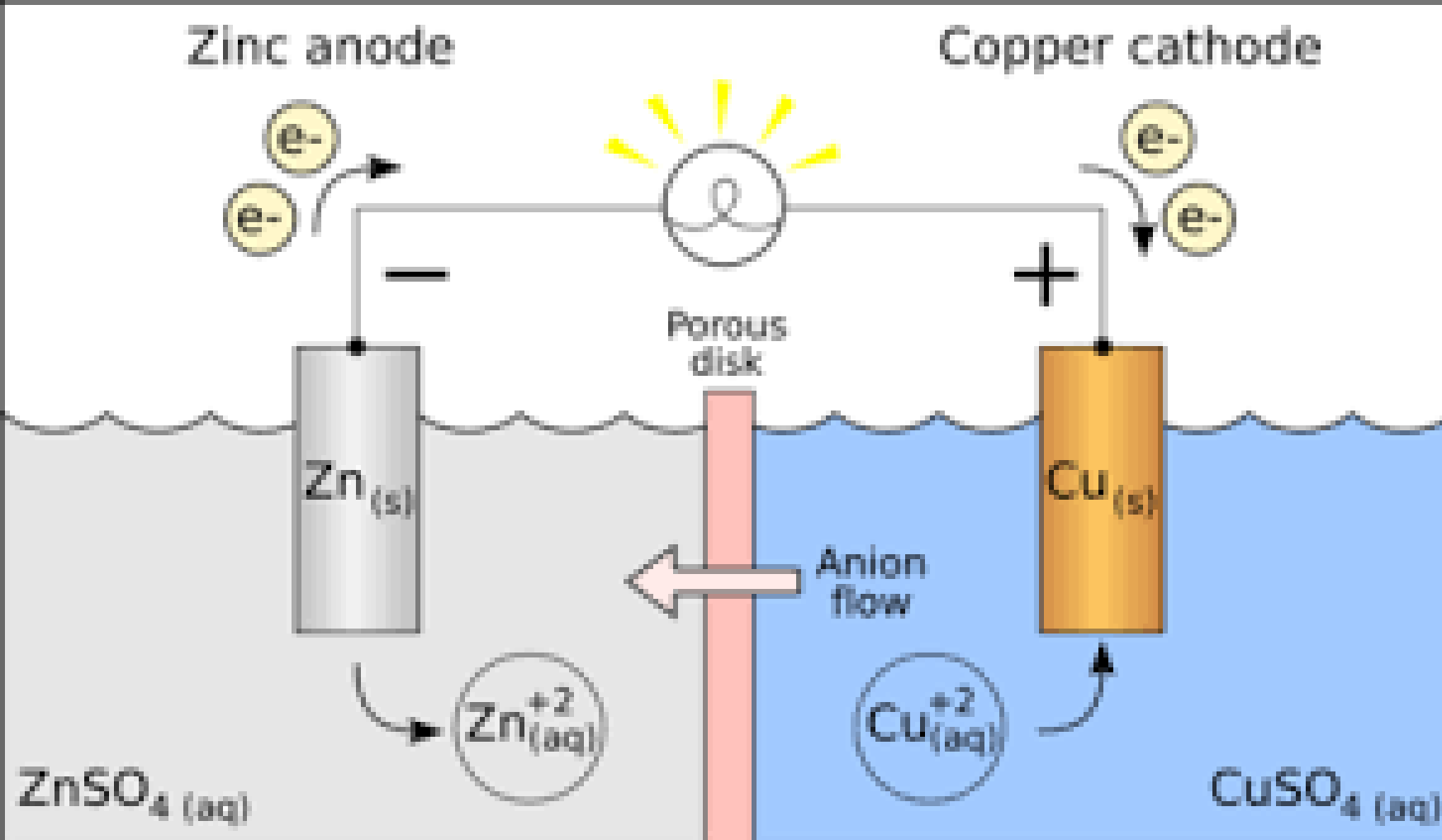
$$Q = \frac{[\text{Oxidation}]}{[\text{Reduction}]}$$

Voltaic Cell Notation

Voltaic cells can be described using a shorthand.
For the cell,



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For a redox reaction in Galvanic Cell. The Nernst equation can be rewritten as:

$$E = E^0 - \frac{0.592V}{n} \log_{10} \frac{[\text{Oxidation}]}{[\text{Reduction}]}$$

See this video for calculation of emf in Non-standard condition using Nernst Equation.

<https://youtu.be/Xgu8WQTaqnQ>

Fig. 1 Galvanic Cell
Oxidation takes place at ANODE (-Ve Electrode, RHS)
Reduction takes place at CATHODE (+Ve Electrode), LHS
Oxidation and Reduction Compartment is separated by porous disk, called SALT BRIDGE (help in to complete the electrical circuits of the cell)

emf & Thermodynamic Relation

The work done

$$W_{\max} = nFE \quad [1]$$

According to Thermodynamics the maximum work obtained from a chemical reaction is equal to the Gibbs free energy for the reaction

$$\Delta G = nFE \quad [2]$$

From equation [1] & [2], we can write

$$\Delta G = nFE \quad [3]$$

According to Gibbs-Helmholtz equation the decrease in free energy of a system at constant pressure is:

$$-\Delta G = -\Delta H - T \left[\frac{\partial(\Delta G)}{\partial T} \right]_p \quad [4]$$

Where $-\Delta H$ is change in heat content of the system. Now substituting the value of ΔG in above equation.

$$nFE = -\Delta H - T \left[\frac{\partial(-nFE)}{\partial T} \right]_p \quad [5]$$

$$nFE = -\Delta H + nFT \left[\frac{\partial E}{\partial T} \right]_p \quad [6]$$

Divide the equation [6] by nF , we have

$$E = \frac{-\Delta H}{nF} + T \left[\frac{\partial E}{\partial T} \right]_p \quad [7]$$

The temperature coefficient of the emf of the cell $\left[\frac{\partial E}{\partial T} \right]$ at constant

emf & Thermodynamic Relation

pressure, therefore, determines whether the electrical energy would be equal to, more or less than the heat of reaction. Accordingly, three cases may arise:

Case I : When the temperature coefficient is zero i.e.,

$$\left[\frac{\partial E}{\partial T}\right]_p = 0, \text{ then,}$$
$$nFE = -\Delta H$$

Case II : When the temperature coefficient is +ve i.e.,

$$\left[\frac{\partial E}{\partial T}\right]_p > 0, \text{ then,}$$
$$nFE > -\Delta H$$

The additional energy will come either from the surroundings or the temperature of the cell would fall.

Case III : When the temperature coefficient is negative i.e.,

$$\left[\frac{\partial E}{\partial T}\right]_p < 0, \text{ then,}$$
$$nFE < -\Delta H$$

The excess energy will be given either to the surroundings or the temperature of the cell would rise

emf & Thermodynamic Relation

If the heat of the reaction (or free energy change) and the temperature coefficient of a cell are known, we can calculate the emf, E , of the cell. For example, in case of a Daniel cell $(\partial E/\partial T)_p$ is nearly zero, $n = 2$ and $\Delta H = -50,100$ Cals.

Since $1 \text{ Cal} = 4.185 \text{ Volt-Coulomb}$,

$$E = \frac{-\Delta H}{nF} = \frac{-4.185(-50,100)}{2(96500)} = 1.09 \text{ V}$$

Thus the emf of Daniel cell is **1.09 volts**. Conversely, if the emf of a reversible cell and its temperature coefficient $(\partial E/\partial T)_p$ are known, ΔH (or ΔG) can be calculated. The heats of reaction calculated from emf measurements are nearly the same as derived from thermal measurements.

emf & Thermodynamic Relation

The relation of entropy with emf can be related as follows:

$$-\Delta S = \left[\frac{\partial(\Delta G)}{\partial T} \right]_p \quad [1]$$

The Gibbs-Helmholtz equation is

$$\Delta G = \Delta H - T\Delta S$$

Then,

$$\Delta G = \Delta H + T \left[\frac{\partial(\Delta G)}{\partial T} \right]_p$$

Upon rearranging the above equation:

$$\frac{\Delta G - \Delta H}{T} = \left[\frac{\partial(\Delta G)}{\partial T} \right]_p$$

We also know that $\Delta G = -nFE$ and putting this value in equation [1]

$$-\Delta S = \left[\frac{\partial(-nFE)}{\partial T} \right]_p$$

$$\Delta S = nF \left[\frac{\partial(E)}{\partial T} \right]_p$$

Lead Storage Battery

What is a Lead-acid Battery?

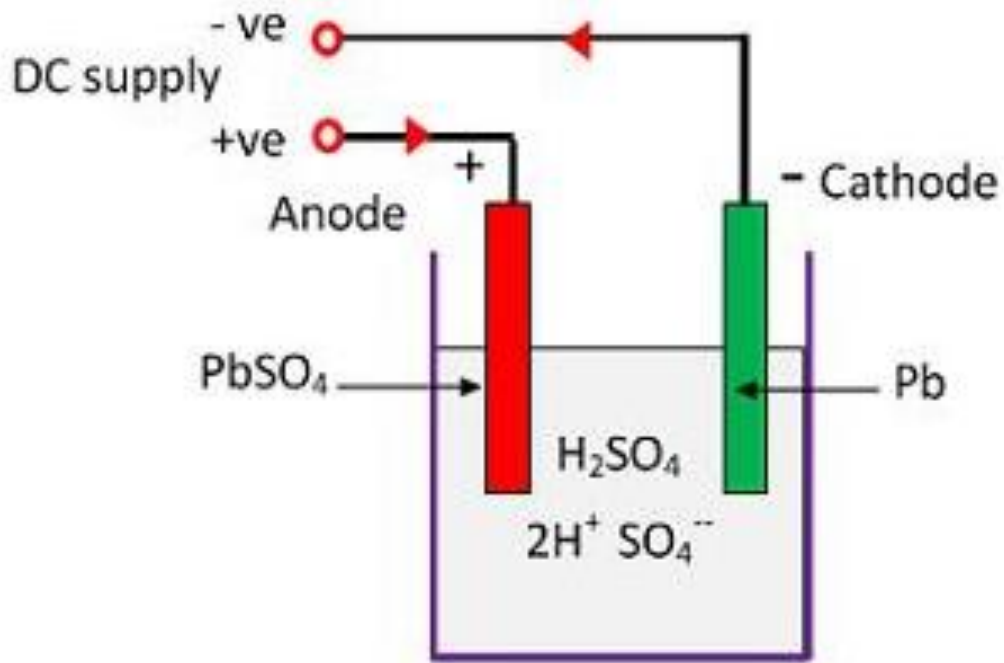
The Lead-acid battery is one of the oldest types of rechargeable batteries. These batteries were invented in the year 1859 by the French physicist Gaston Plante.

Lead-acid batteries can be classified as secondary batteries. The chemical reactions that occur in secondary cells are reversible. The reactants that generate an electric current in these batteries (via chemical reactions) can be regenerated by passing current through the battery (recharging).

The chemical process of extracting current from a secondary battery (forward reaction) is called **discharging**. The method of regenerating active material is called **charging**. A typical Lead-Storage Battery is:

- ❖ A typical 12-V lead-acid battery has six cells connected in series, each of which delivers about 2 V.
- ❖ Each cell contains two **lead grids** packed with the electrode material

- | | |
|-------------------|---|
| A. Anode (+Ve) : | Spongy Pb |
| B. Cathode (-Ve): | PbO ₂ . |
| C. Electrolyte : | 4.5 M H ₂ SO ₄ (solution) |

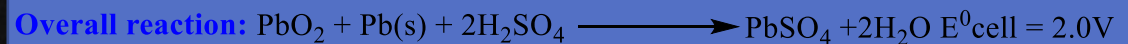


Lead-Acid Battery Charging

What is a Lead-acid Battery?

Fiberglass sheets between the grids prevents shorting by accidental physical contact.

When the cell discharges, it generates electrical energy as a voltaic cell.



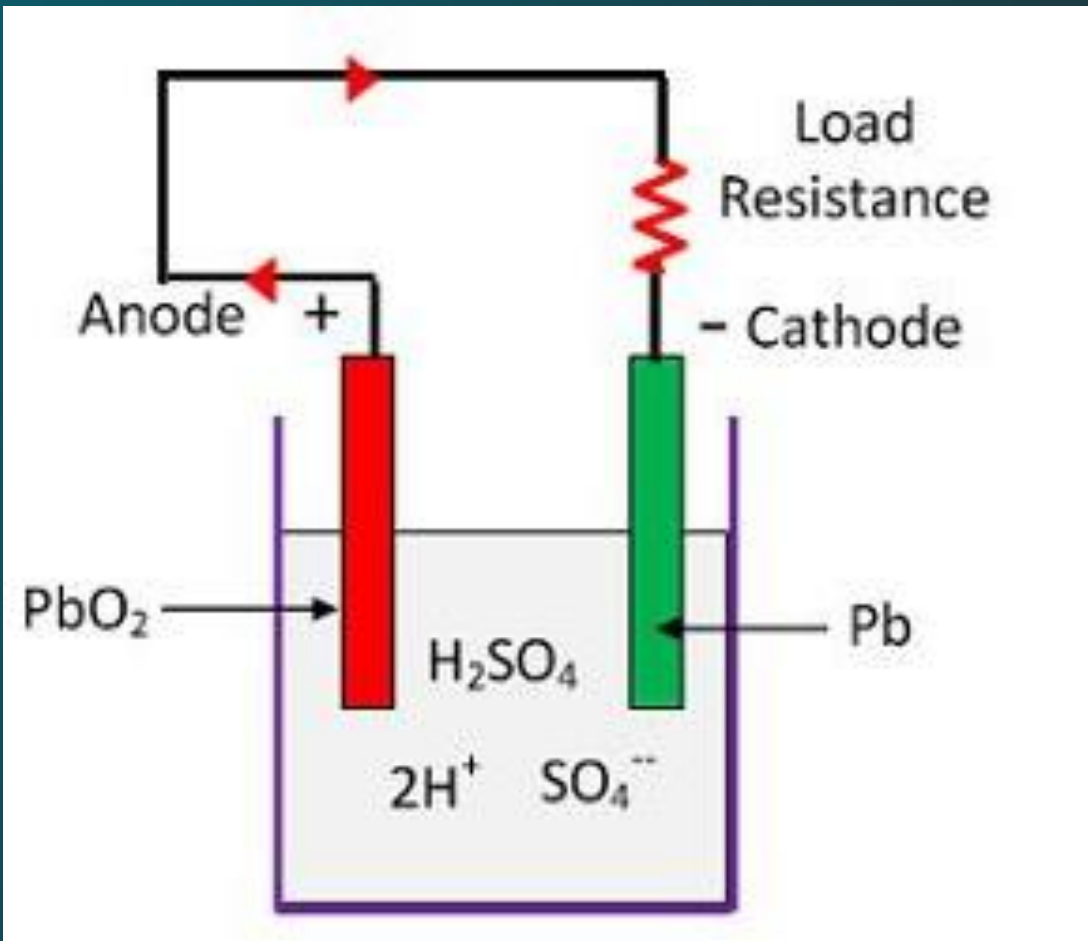
Note that both half-reaction produce Pb^{2+} ion, one through oxidation of Pb, the other through reduction of PbO_2 .

At both electrodes, the Pb^{2+} react with SO_4^{2-} to form $\text{PbSO}_4\text{(s)}$

What happens as all the amps get used up?

The electrolyte turns to water and the lead and sponge lead plates turn to Lead sulfate and the acid will no longer strip electrons from the positive plates and add them to the negative plates

The battery will go DEAD.



What happens as all the amps get used up?

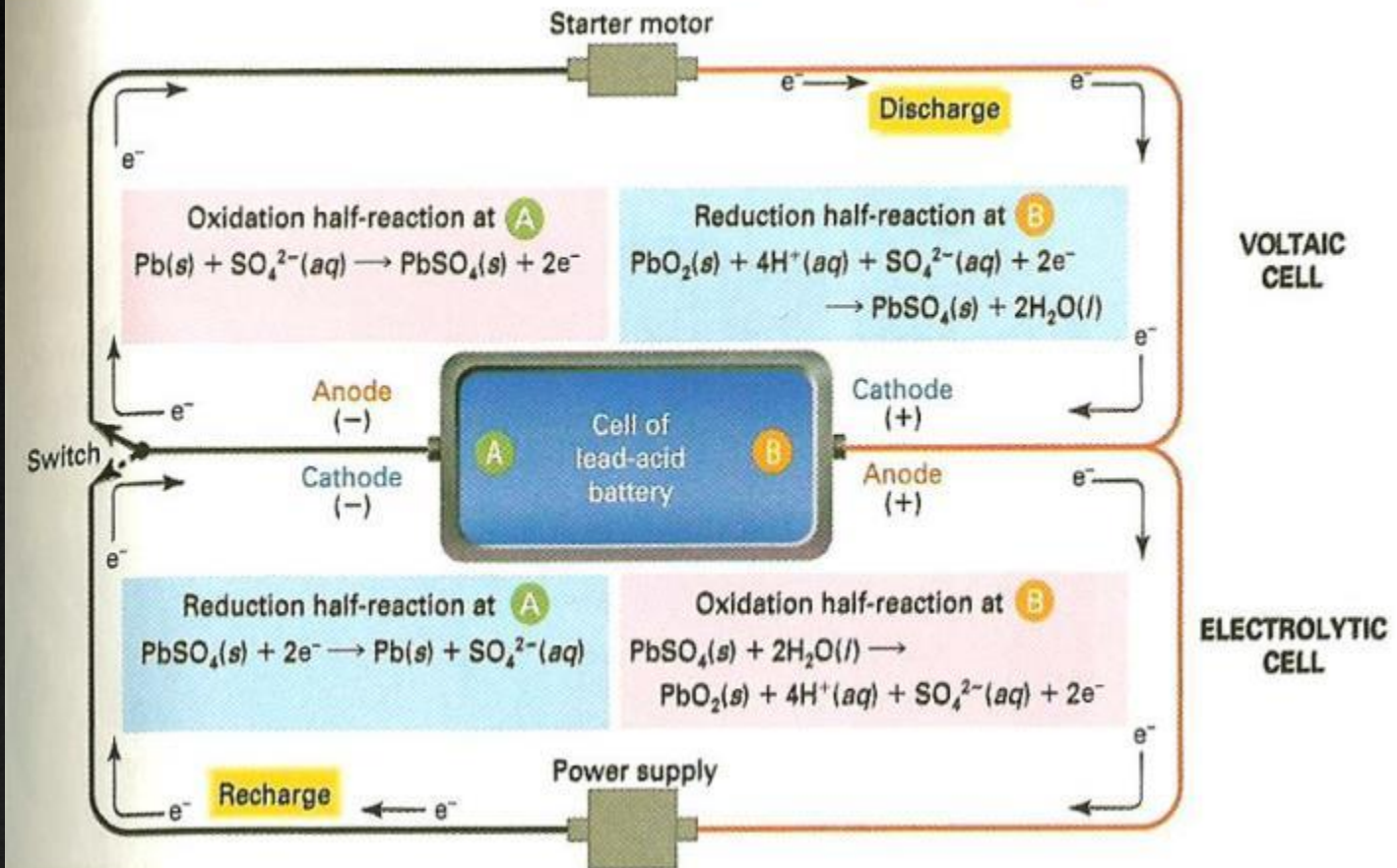
NOTE: Add distilled (or de-mineralized) water to the low electrolyte battery. Adding tap water will encourage electrolysis. This will speed up the loss of that water when charging and discharging. It will also encourage corrosion on the battery cables.

Lead-Acid Battery Discharging

What is a Lead-acid Battery?

Lead Storage Battery Summary

Lead Storage Battery



CORROSION

What is a Corrosion?

It is defined as the natural process that causes the transformation of pure metals to undesirable substances when they react with substances like water or air. This reaction causes damage and disintegration of the metal starting from the portion of the metal exposed to the environment and spreading to the entire bulk of the metal. This is a natural Oxidation process by which the metal is Oxidized into its corresponding stable form of Oxide.

Note: Interestingly, aluminium doesn't corrode unlike other metals even though it is reactive. This is because aluminium is covered by a layer of aluminium oxide already. This layer of aluminium oxide protects it from further corrosion.

CORROSION

What are the Factors influencing Corrosion?

- ❖ Exposure of the metals to air containing gases like CO_2 , SO_2 , SO_3 etc.
- ❖ Exposure of metals to moisture especially salt water (which increases the rate of corrosion).
- ❖ Presence of impurities like salt (e.g. NaCl)
- ❖ Temperature: An increase in temperature increases corrosion.
- ❖ Presence of acid in the atmosphere: acids can easily accelerate the process of corrosion.

CORROSION

Types of Corrosion

Following are the 9 different types of corrosions that commonly occur in metals.

1. Atmospheric Corrosion
2. Erosion Corrosion
3. Selective Corrosion
4. Uniform Corrosion
5. Pitting Corrosion
6. Fretting Corrosion
7. Stress Corrosion
8. Inter-granular Corrosion
9. Corrosion Fatigue

CORROSION

Corrosion of Iron (Rusting):

Various theories had been advanced to explain corrosion from time to time. The modern view, known as the electrochemical theory of corrosion, appears to be sounder. This theory is described below by taking the example of rusting of iron.

Water containing oxygen and carbon dioxide acts as an electrolyte and helps in flow of electrons.

The formation of rust on the surface of iron occurs through the following steps.

❖ **At the anodic region.** Iron in contact with water forms anode and gets oxidized to Fe^{2+} .

Anodic region: $\text{Fe(s)} \rightarrow \text{Fe}^{2+}(\text{aq}) + 2\text{e}^-$ $E^\circ \text{Fe}^{2+}/\text{Fe} = -0.44 \text{ V}$

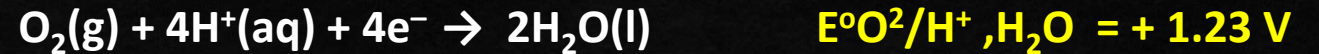
The released electrons move to another portion of the iron sheet. This portion of the iron sheet serves as cathode.

❖ **At the cathodic region.** At this cathodic portion of the surface, oxygen in the presence of H^+ ions (produced due to the ionization of water molecules) get reduced to form H_2O .

CORROSION

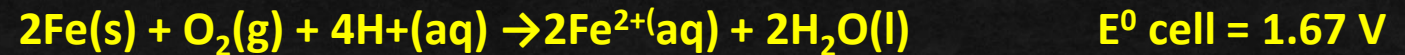
Corrosion of Iron (Rusting):

Cathodic region:



The overall reaction of the local cell is the sum of the cathodic and anodic reactions.

Overall cell reaction:



Fe²⁺ ions move through the water on the surface of the iron sheet. Presence of electrolytes (e.g., sodium chloride, SO₂, CO₂ etc.) in water helps in carrying more current through the local cell on the surface of iron. The increased flow of current enhances the rate of corrosion. The Fe²⁺ ions are further oxidized by atmospheric oxygen to Fe³⁺, and form hydrated iron(III) oxide, expressed as Fe₂O₃.xH₂O. The hydrated ferric oxide is called rust.

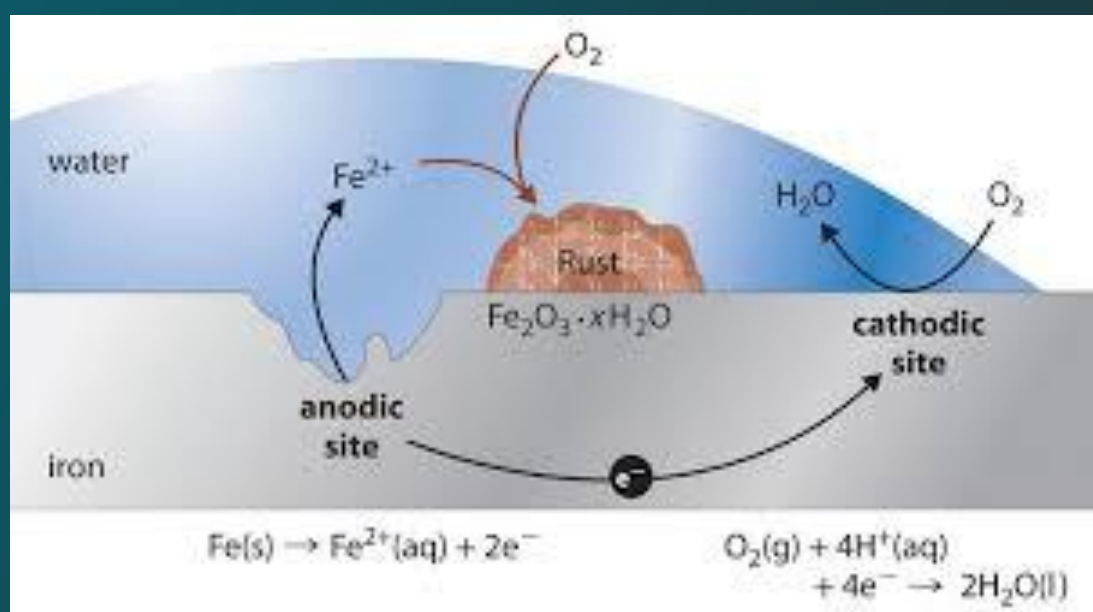
Corrosion of Iron (Rusting):



H⁺ ions produced in the above reaction help further in the rusting of iron. Impurities present in iron also enhance rusting by setting several localized cells. Pure iron does not rust.

You may go through the video below to understand the basics of Electrochemical Corrosion:

<https://youtu.be/-tTNrgLUdYs>



Electrochemical theory of Corrosion

Corrosion Control & Prevention

Corrosion prevention technique can be generally classified into Six group:

- ❖ Environmental modifications
- ❖ Metal selection and surface conditions
- ❖ Cathodic protection
- ❖ Corrosion inhibitors
- ❖ Coating
- ❖ Plating

Corrosion Control & Prevention

Environmental modifications:

The modification of the environment consist to reduce or eliminate the corrosive agents which is under the part or structure to be protected. Basically it is used corrosion inhibitors, sequestrants and pH modifiers as techniques or methods to modify the environment.

Corrosion Control & Prevention

Metal selection and surface conditions:

One simple way to prevent corrosion is to use a corrosion resistant metal such as aluminum or stainless steel. Depending on the application, these metals can be used to reduce the need for additional corrosion protection.

Corrosion Control & Prevention

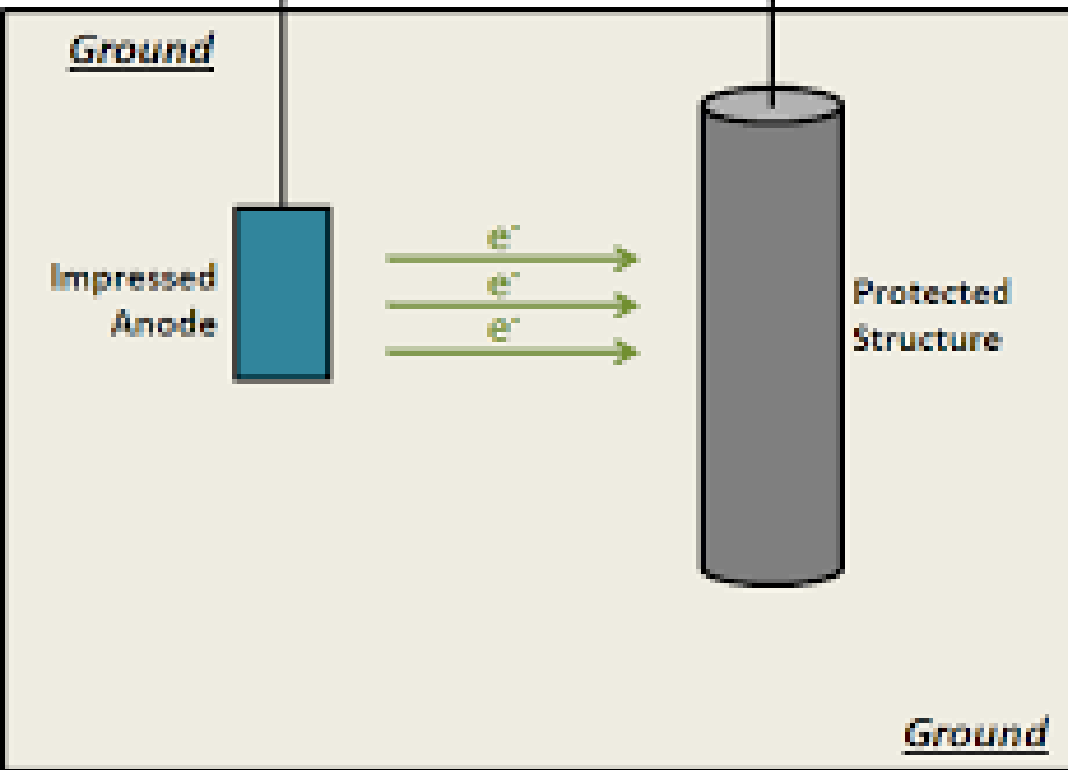
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Prevention of Corrosion

Cathodic protection (CP) is a technique used to control the **corrosion** of a metal surface by making it the cathode of an electrochemical cell. A simple method of **protection** connects the metal to be **protected** to a more easily **corroded** "**sacrificial metal**" to act as the anode.

Example: Mg, Al etc.



Cathodic Protection

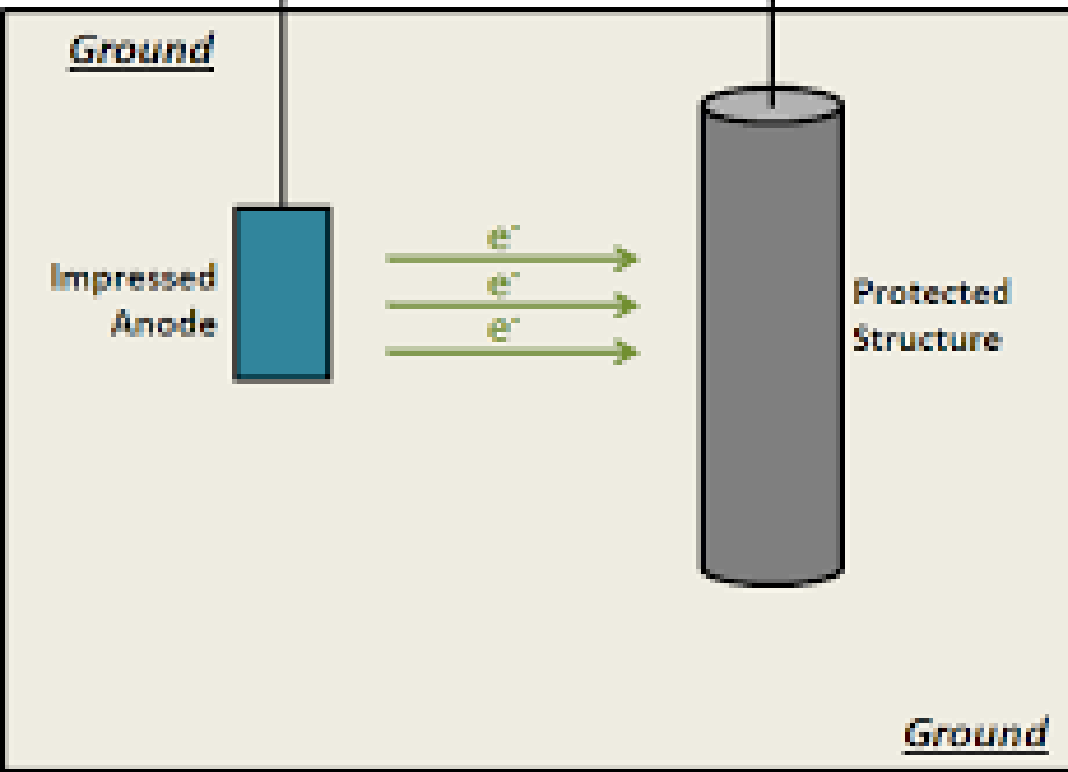
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Example: Mg, Al, Zn etc.

Application:

- ❖ Protection of buried pipeline
- ❖ Underground cables
- ❖ Marine structure (Ship)
- ❖ Ship hulls
- ❖ Water tanks
- ❖ Pipes.



Cathodic Protection

Prevention of Corrosion

Anodic Protection

Anodic protection (AP):

Anodic protection involves coating the iron alloy steel with a less active metal, such as tin. Tin will not corrode, so the steel will be protected as long as the tin coating is in place. This method is known as anodic protection because it makes the steel the anode of an electrochemical cell.

Protecting Coating

The application of a paint coating is a cost-effective way of preventing corrosion. Paint coatings act as a barrier to prevent the transfer of electrochemical charge from the corrosive solution to the metal underneath.

Another possibility is applying a powder coating. In this process, a dry powder is applied to the clean metal surface. The metal is then heated which fuses the powder into a smooth unbroken film. A number of different powder compositions can be used, including acrylic, polyester, epoxy, nylon, and urethane.

Corrosion Inhibitors

Corrosion Inhibitors

Corrosion inhibitors are chemicals that react with the surface of the metal or the surrounding gases to suppress the electrochemical reactions leading to corrosion. They work by being applied to the surface of a metal where they form a protective film. Inhibitors can be applied as a solution or as a protective coating using dispersion techniques. Corrosion inhibitors are commonly applied via a process known as passivation.

Passivation

In passivation, a light coat of a protective material, such as metal oxide, creates a protective layer over the metal which acts as a barrier against corrosion. The formation of this layer is affected by environmental pH, temperature, and surrounding chemical composition. A notable example of passivation is the Statue of Liberty, where a blue-green patina has formed which actually protects the copper underneath. Corrosion inhibitors are used in petroleum refining, chemical production, and water treatment works.



COVID-19 Safety & Prevention

❖ Clean your hands often

❖ Avoid close contact

❖ Cover your mouth and nose



There is currently no vaccine to prevent coronavirus disease 2019 (COVID-19)

COVID-19 Safety & Prevention

❖ Cover coughs and sneezes

❖ Clean and disinfect

The best way to prevent illness is to avoid being exposed to this virus.

Downloads the Aarogya Setu apps

<https://www.mygov.in/aarogya-setu-app/>

**Thank you
For
Watching**

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