

1. ➤ Nernst equation- derivation, explanation, importance
2. ➤ Measurement of EMF
3. ➤ Primary and Secondary batteries differences.
4. ➤ Advantages of using fuel cells over traditional batteries.
5. ➤ Construction, working, and applications of SHE with suitable examples.
6. ➤ Electrochemical series- definition, explanation and applications/ uses.
7. ➤ Concentration cells- working principle.
8. ➤ Hydrogen-oxygen fuel cell- working, applications.
9. ➤ methanol-oxygen fuel cell- working, applications.
10. ➤ Lead acid battery- working, reactions, applications.
11. ➤ Nickel-Metal Hydride (NiMH) cells- working, reactions, applications.
12. ➤ Working and applications of Li-ion batteries.
13. ➤ Construction and working of calomel electrodes with an example.
14. ➤ Determination of pH of a given unknown sample.
15. ➤ Pitting corrosion- causes and mechanism.
16. ➤ Factors influencing rate of corrosion.
17. ➤ Wet theory(Electro chemical corr) of corrosion- mechanisms and effects on materials.
18. ➤ Sacrificial anodic method
19. ➤ Impressed current cathode method
20. ➤ Theories of chemical and electrochemical corrosion
21. ➤ Cathodic protection works and illustrate the impressed current method- reactions.
22. ➤ Electroplating process.
23. ➤ Differences between cathodic coatings and anodic coatings.
24. ➤ Chemical theory of corrosion and its types with suitable examples.
25. ➤ Galvanic corrosion and its mechanism
26. ➤ Differential aeration corrosion mechanism with suitable examples.

Answers:

3.4.3 Comparison of sacrificial anode method with impressed current cathodic method

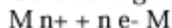
Table 3.1

No.	Sacrificial anode method	Impressed current method
1.	External power supply is not required.	External power supply is required.
2.	Investment is low.	Investment is high.
3.	This requires periodic replacement of sacrificial anode.	Replacement is not required as anodes are stable.
4.	Soil and microbiological corrosion effects are not considered.	Soil and microbiological corrosion effects are taken into account.
5.	This is the most economical method especially when short term protection is required.	This is well suited for large structures and long term operation.
6.	This is a suitable method when the current requirement and the resistivity of the electrolytes are relatively low.	This is a suitable method even when the current requirement and the resistivity of the electrolytes are high.

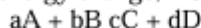
1)

Nernst Equation

Consider a general redox reaction,



For a general reversible chemical reaction, according to Vant-Hoff's isotherm, Gibb's free energy change, ΔG of the reaction and its equilibrium



and is given by,

$$\Delta G = -RT \ln K + RT \ln [\text{Product} / \text{Reactant}] \dots\dots\dots 1$$

$$\text{We know that } \Delta G^0 = -RT \ln K$$

Substituting the above in Van't - Haff's isotherm equation,

$$\Delta G = \Delta G^0 + RT \ln [\text{Product} / \text{Reactant}] \dots\dots\dots 2$$

Where ΔG^0 = Standard free energy change.

For reversible reaction involving M electrons, the decrease in free energy ($-\Delta G$) will produce electrical energy (E) coulombs and is given by

$$nFE = -\Delta G$$

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

$$\text{or } -\Delta G^0 = nFE^0 \dots\dots\dots 3$$

ΔG^0 = Standard free energy change

n = the number of electrons

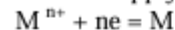
F = Faraday = 96,500 Coulombs of electricity

E^0 = the standard potential.and

Substituting Eq. (3) in Eq. (2), we get,

$$-nFE = -nFE^0 + RT \ln [M]/[M^{n+}] \dots\dots\dots 4$$

When we apply this equation to an electrode reduction equation



We get,

$$-nFE_{\text{red}} = -nFE^0_{\text{red}} + RT \ln [M]/[M^{n+}]$$

Rearranging the above equation, we get

$$E_{\text{red}} = E^0_{\text{red}} - RT/nF \ln [M]/[M^{n+}]$$

$$E_{\text{red}} = E^0_{\text{red}} - RT/nF \ln [1]/[M^{n+}] \text{ (since } [M] = 1 \text{ the activity of the solid metal)}$$

The above equation may be written as,

$$E_{\text{red}} = E^0_{\text{red}} + RT/nF \ln [M^{n+}]$$

where $R = 8.314 \text{ J/K/mole}$, $T = 2980 \text{ K}$, $F = 96500 \text{ coulombs}$. Now substituting the value of R , T and F we get,

$$E_{\text{red}} = E^0_{\text{red}} + 0.0591/n \log [M^{n+}] \dots\dots\dots 5$$

The above equation is known as the **Nernst** Equation.

In general,

$$E = E^0_{\text{red}} + 0.0591/n \log C \dots\dots\dots 6$$

Similarly for oxidation potential,

$$E = E^0_{\text{oxi}} - 0.0591/n \log [M^{n+}] \dots\dots\dots 7$$

The Eqs (5) and (7) are known as **Nernst** Equation for single electrode potential.

Thermodynamics of cell reactions

Free energy & Electrical work

Free energy and potential in electrochemical cells are related in the following way:

$$\Delta G = -nFE_{cell}$$

n = mol of e^- transferred

F is the Faraday constant = 9.65×10^4 J/V·mol

Cell potential (E°_{cell})

When both reactants and products are in their standard states, the relationship between ΔG° and E°_{cell} is as follows:

$$\Delta G^\circ = -nFE^\circ_{cell}$$

Spontaneous redox reaction;

Positive E°

Negative; ΔG

Non-Spontaneous redox reaction;

Negative E°

Positive ΔG

Free energy & Electrical work

The following equation relates the standard free-energy change to the equilibrium constant:

$$\Delta^\circ = -RT \ln k$$

Based on the relationship between the standard free-energy change and the standard cell potential, we can write

$$-nFE^\circ_{cell} = -RT \ln k$$

By rearranging this equation, $E^\circ_{cell} = \frac{RT}{nF} \ln k$

For $T=298K$, the equation can be simplified as follows:,

$$E^\circ_{cell} = \frac{0.0592 V}{n} \log k$$

Nernst equation

Following the connection between free energy and cell potentials, non-standard concentrations follow. Recall that

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Where Q is the reaction quotient

Converting to cell potentials:

$$-nFE_{cell} = -nFE^\circ_{cell} + RT \ln Q$$

or

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln Q$$

It is a generalized Nernst equation that can be applied to any temperature.

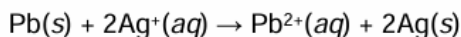
Rewriting it as follows simplifies it for reactions occurring at 25 °C (298.15 K)

$$E_{cell} = E^\circ_{cell} - \frac{0.0592 V}{n} \log k$$

Sample Problem

Calculating K and ΔG° from E°_{cell}

PROBLEM: Lead can displace silver from solution, and silver occurs in trace amounts in some ores of lead.

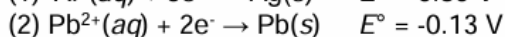
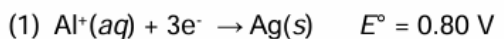


Therefore, silver is a valuable byproduct in the industrial extraction of lead from its ore. Calculate K and ΔG° at 298.15 K for this reaction.

PLAN: ✓ We divide the spontaneous redox reaction into the half-reactions.
 ✓ Use values from Appendix D to calculate E°_{cell} .
 ✓ From this we can find K and ΔG° .

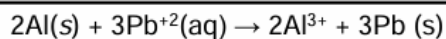
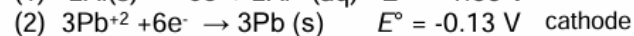
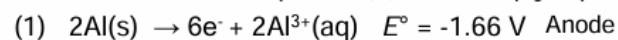
SOLUTION:

Writing the half-reactions with their E° values:



Sample Problem Solution

We need to reverse equation (2) and multiply equation (1) by 2:



$$E^\circ_{\text{cell}} = -0.13 - (-1.66) = 1.53 \text{ V}$$

$$E^\circ_{\text{cell}} = \frac{0.0592 \text{ V}}{6} \log K$$

$$\log K = \frac{1.53 \text{ V} \times 6}{0.0592 \text{ V}} = 154.80 \quad \boxed{K = 10^{154.8}}$$

$$\Delta G^\circ = -nFE^\circ_{\text{cell}} = - \frac{6 \text{ mol e}^-}{\text{mol}_{\text{rxn}}} \times \frac{96.5 \text{ kJ}}{\text{V} \cdot \text{mol e}^-} \times 1.53 \text{ V}$$

$$= -8.8 \times 10^2 \text{ kJ/mol}_{\text{rxn}}$$

Sample Problem**Calculating the Potential of a Concentration Cell**

PROBLEM: A concentration cell consists of two Ag/Ag⁺ half-cells. In half-cell A, the electrolyte is 0.0100 M AgNO₃; in half-cell B, it is 4.0 × 10⁻⁴ M AgNO₃. What is the cell potential at 298.15 K?

Nernst Equation

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{nF} \ln Q$$

- When $Q < 1$, [reactant] > [product], $\ln Q < 0$, so $E_{\text{cell}} > E^{\circ}_{\text{cell}}$
- When $Q = 1$, [reactant] = [product], $\ln Q = 0$, so $E_{\text{cell}} = E^{\circ}_{\text{cell}}$
- When $Q > 1$, [reactant] < [product], $\ln Q > 0$, so $E_{\text{cell}} < E^{\circ}_{\text{cell}}$

We can simplify the equation as before for $T = 298.15 \text{ K}$:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592 \text{ V}}{n} \log Q$$

1. Given:

- $[Ag^+]_A = 0.0100 \text{ M}$, $[Ag^+]_B = 4.0 \times 10^{-4} \text{ M}$
- $E^{\circ}_{\text{cell}} = 0 \text{ V}$, $n = 1$, $T = 298.15 \text{ K}$

2. Nernst Equation:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592}{n} \log Q$$

$$\text{Where } Q = \frac{[Ag^+]_B}{[Ag^+]_A} = \frac{4.0 \times 10^{-4}}{0.0100} = 0.04.$$

3. Substituting values:

$$E_{\text{cell}} = 0 - 0.0592 \times \log(0.04)$$

$$\log(0.04) = -1.398$$

4. Calculation:

$$E_{\text{cell}} = 0 - 0.0592 \times (-1.398)$$

$$E_{\text{cell}} = 0.0827 \text{ V}$$

Answer:

The cell potential is **0.0827 V**.

Applications of Nernst Equation:

Electrode potential of unknown metal can be determined using the Nernst equation.

It is used to predict the corrosion tendency of metals.

Problems:

(1) Calculate the reduction potential of Cu/Cu²⁺ electrode which is dipped in 0.5M of its own salt solution at 25°C and the standard electrode potential of its is 0.337.

Find out the emf.

$$E = E^{\circ} + \frac{0.0591}{n} \log (Cu^{2+}) \text{ Volts } n=2 ;$$

$$\text{(Ans): Reduction Potential} = 0.3230 \text{ V}$$

(2) Find out the oxidation potential of Zn/Zn²⁺ which is in contact with 0.2 M of its own salt solution at 25°C and the std. electrode potential is 0.763 V.

$$E = E^{\circ} + \frac{0.0591}{n} \log (Zn^{2+}) \text{ V } n=2;$$

$$\text{(Ans) : Oxidation potential} = 0.7836 \text{ V}$$

Problem 1: Calculating the Reduction Potential of Cu/Cu²⁺:

Given Data:

- Standard electrode potential (E°) = 0.337 V
- Concentration of Cu²⁺ ion ($[Cu^{2+}]$) = 0.5 M
- Temperature = 25°C (298.15 K)
- Number of electrons transferred (n) = 2
- Formula:

$$E = E^{\circ} + \frac{0.0591}{n} \log [Cu^{2+}]$$

Substituting Values:

$$E = 0.337 + \frac{0.0591}{2} \log [0.5]$$

First, calculate $\log[0.5]$:

$$\log[0.5] = \log[5 \times 10^{-1}] = \log 5 + \log 10^{-1}$$

$$\log[0.5] = 0.698 - 1 = -0.301$$

Now substitute back into the equation:

$$E = 0.337 + \frac{0.0591}{2} \times (-0.301)$$

$$E = 0.337 - 0.0089$$

$$E = 0.323 \text{ V}$$

Answer:

The reduction potential of Cu/Cu²⁺ = 0.3230 V

Problem 2: Calculating the Oxidation Potential of Zn/Zn²⁺:

Given Data:

- Standard electrode potential (E°) = -0.763 V
(Note: Given standard potential is for reduction, and oxidation is its reverse, so the sign will flip to 0.763 V)
- Concentration of Zn²⁺ ion ($[Zn^{2+}]$) = 0.2 M
- Temperature = 25°C (298.15 K)
- Number of electrons transferred (n) = 2
- Formula:

$$E = E^{\circ} + \frac{0.0591}{n} \log [Zn^{2+}]$$

Substituting Values:

$$E = 0.763 + \frac{0.0591}{2} \log [0.2]$$

First, calculate $\log[0.2]$:

$$\log[0.2] = \log[2 \times 10^{-1}] = \log 2 + \log 10^{-1}$$

$$\log[0.2] = 0.301 - 1 = -0.699$$

Now substitute back into the equation:

$$E = 0.763 + \frac{0.0591}{2} \times (-0.699)$$

$$E = 0.763 - 0.0207$$

$$E = 0.7836 \text{ V}$$

Electrochemical Cells, Reversible and Irreversible cells and Cell EMF

Electro Chemical Cell:
An electrochemical cell is a device, which is used to convert chemical energy into electrical energy and vise versa.
These electrochemical cells are classified into two types as follows.

1) Galvanic or Voltaic cells (Reversible): These are the electrochemical cells, which convert chemical energy into electrical energy.

Ex: Daniel cell, Dry cell, etc.

2) Electrolytic cell (Irreversible): These are the electrochemical cells, which are used to convert electrical energy into chemical energy.

Ex: Lead acid battery, Nickel cadmium battery etc.,

Electron Motive Force (EMF)

It is defined as the potential difference between the two electrodes of a galvanic cell which causes the flow of current from an electrode with higher reduction potential to the electrode with lower reduction potential. It is denoted as E cell.

E cell = E right –E left.

E cell = E cathode – E anode.

Problems:

1) Calculate emf of a cell constructed by combining Cu & Zn electrodes dipping in their respective ionic solutions. The standard electrode potential of Cu and Zn are 0.34 V and 0.76 V respectively at 298K.

E cell = E cathode – E anode = Ecu – Ezn = 0.34 – (-0.76) = 1.1volt

Electromotive force (EMF) can be measured in a few ways:

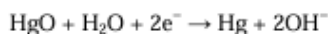
- **Use a voltmeter:** Measure the voltage across the cell
- **Use an ammeter:** Measure the current in the circuit
- **Use a potentiometer:** A preferred method for measuring a cell's EMF
- **Connect to a circuit:** Connect the battery to a circuit with a resistor, voltmeter, and ammeter. The EMF is the sum of the voltage differences across the resistor and the battery.

EMF is the energy transferred to an electric circuit per unit of electric charge. It is measured in volts.

3)

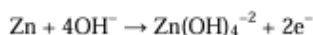
Feature	Primary Batteries	Secondary Batteries
Definition	Non-rechargeable; used once and discarded.	Rechargeable; can be used multiple times.
Energy Conversion	Converts chemical energy to electrical energy.	Acts as both a voltaic cell (discharging) and an electrolytic cell (charging).
Examples	Mercury battery, Alkaline battery.	Lead-acid battery, Nickel-metal hydride (NiMH) battery.
Electrode Materials	Often involves single-use materials like zinc and mercuric oxide.	Designed with durable materials like lead and nickel.
Application	Low-power devices like watches, calculators.	High-power applications like cars, UPS systems, and industrial uses.
Cost	Generally cheaper.	Higher initial cost but cost-effective over time.
Life Cycle	Single-use only.	Can endure several charge-discharge cycles.
Environmental Impact	Generates more waste due to single-use nature.	Reduced waste due to reusability.
Primary batteries like the mercury battery are ideal for low-energy applications where rechargeability is unnecessary, while secondary batteries like lead-acid and NiMH batteries dominate in applications requiring repeated use and higher energy storage capacity.		

oxide is a non-conductor, so some graphite is mixed with it; the graphite also helps prevent collection of mercury into large droplets. The half-reaction at the cathode is:



with a standard potential of +0.0977 V vs. NHE.

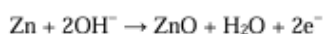
The anode is made of zinc (Zn) and separated from the cathode with a layer of paper or other porous material soaked with electrolyte; this is known as a salt bridge. Two half-reactions occur at the anode. The first consists of an electrochemical reaction step:



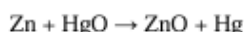
followed by the chemical reaction step:



yielding an overall anode half-reaction of:



The overall reaction for the battery is:



In other words, during discharge, zinc is oxidized (loses electrons) to become zinc oxide (ZnO) while the mercuric oxide gets reduced (gains electrons) to form elemental mercury. A little extra mercuric oxide is put into the cell to prevent evolution of hydrogen gas at the end of life.

Secondary Battery (Lead Acid and Nickel metal hydride)

Storage cell: it is the one which can act both as voltaic cell and electrolytic cell. When it functions as voltaic cell, it supplies electric current and the process is known as discharging. When it functions as electrolytic cell, it receives electric current and this process is known as charging. So it can be used for a large no. of cycles of charging and discharging. The best example for storage cell is lead acid battery or lead acid accumulator.

1. Lead-acid battery: Lead-acid is the oldest rechargeable battery in existence. Invented by the French physician Gaston Planté in 1859, lead-acid was the first rechargeable battery for commercial use. 150 years later, we still have no cost-effective alternatives for cars, wheelchairs, scooters, golf carts and UPS systems.

Construction: Large number of anodes and cathodes are arranged alternatively in a series separated by insulators as shown above. The entire set up is immersed in dilute sulphuric acid solution.

Primary Cell (Mercury Battery)

Mercury batteries use either pure mercury (II) oxide (HgO)—also called mercuric oxide—or a mixture of HgO with manganese dioxide (MnO₂) as the cathode. Mercuric

Anode: lead plate

Cathode: lead dioxide plate

Electrolyte: 25% H₂SO₄ solution

4)

Fuel Cell vs. Battery

- Battery; Energy storage device
 - Reactant chemicals already in device
 - Once Chemicals used up; discard (unless rechargeable)
- Fuel Cell; Energy conversion device
 - Won't work unless reactants supplied
 - Reactants continuously supplied; products continuously removed

Fuel cells have several advantages over traditional batteries, including:

- **Refueling time:** Fuel cells can be refueled in minutes, while batteries can take hours to recharge.
- **Temperature tolerance:** Fuel cells are less sensitive to cold temperatures than batteries.
- **Energy density:** Fuel cells have a higher energy density by weight than batteries.
- **Efficiency:** Fuel cells are often more efficient than traditional batteries.

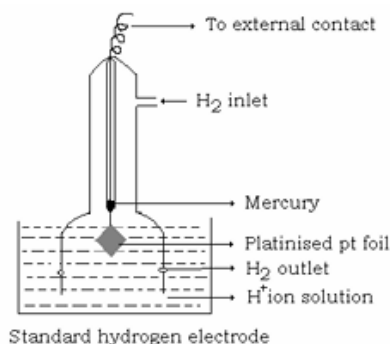
- **Reliability:** Fuel cells are a dependable energy source because hydrogen stored as a gas or liquid remains ready for use.
- **Environmental impact:** Fuel cells produce minimal emissions, only water vapor and heat.
- **Noise pollution:** Fuel cells do not generate excessive noise.
- **Renewable:** Hydrogen is the most abundant element on earth.

Fuel cells convert an energy source, such as hydrogen, propane, diesel, or natural gas, into electrical energy. Batteries, on the other hand, store energy.

1. **Higher Energy Efficiency:** Fuel cells convert chemical energy directly into electrical energy, which can result in higher efficiency compared to batteries that involve multiple energy conversion steps.
2. **Longer Runtime:** Fuel cells can operate continuously as long as fuel (like hydrogen) is supplied, whereas batteries have a limited capacity and need recharging once depleted.
3. **Lower Emissions:** Fuel cells typically produce fewer emissions than conventional batteries, especially when using hydrogen, which only emits water vapor as a byproduct.

5)

Construction, working and limitations of standard hydrogen electrode



The standard hydrogen electrode consists of platinised platinum foil fused to the glass tube. Mercury is placed at the bottom of the tube and a copper wire is used for electrical connections. The platinum foil is immersed in a solution containing unit

molar hydrogen ions. Pure hydrogen gas is bubbled about the electrode through the H_2 gas inlet at 1atm pressure.

The electrode is represented as $Pt/H_2(g)/H^+$

If the concentration of H^+ is 1M, H_2 gas bubbled at 1atm pressure and at temperature 298K, then the electrode is called standard hydrogen electrode. And the electrode potential is arbitrarily fixed as zero.

The electrode reaction is:

Limitations of SHE

- i) The construction of SHE is difficult.
- ii) It is very difficult to maintain the concentration of H^+ as 1M and Pressure H_2 gas at 1atm
- iii) Platinum electrode is poisoned by the impurities of the gas
- iv) It cannot be used in the presence of oxidizing agents.

Applications of SHE include its use in determining standard electrode potentials for various half-reactions, providing a basis for electrochemical measuring instruments, and facilitating pH measurements in analytical chemistry. For example, when considering the cell potential in galvanic cells, the SHE is frequently used as the reference point.

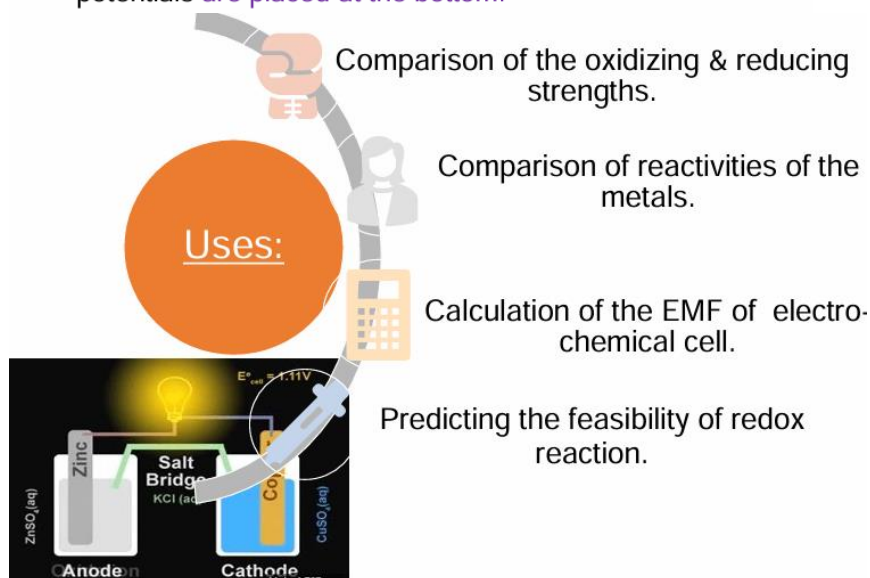
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Electrochemical Series

- Created by comparing different electrode potentials to conventional **SHE**, it helps in the arrangement of electrodes.
- It describes the arrangement of electrode in order of their increasing potential values.

Features:

- All reduction potentials are given on hydrogen scale.
- When an electrode has a greater potential, it is easier to reduce it.
- Oxidation is easier for electrode with low potential.
- A high (+ve) electrode potential is placed at the top of the EMF series. In contrast, those with a lower (-ve) electrode potentials are placed at the bottom.



Electrochemical Series



Comparison of the relative oxidizing & reducing strengths

- Selection of **Anode** & **Cathode** in a cell.
- Identify good reducing & oxidation agents.

- Electrode having lower potential/negative value is **Anode; Reducing agent**.
- Electrode having higher potential/positive value is **Cathode; Oxidizing agent**.

examples

Zn (-0.76 V)	Au (+1.50 V)	Zn (-0.76 V)	Cu (+0.34 V)
Anode	Cathode	Anode	Cathode
Ni (-0.25 V)	Ag (+0.80 V)	Al (-1.66 V)	Cu (+0.34 V)
Anode	Cathode	Anode	Cathode

Half Reaction	Standard Potential (V)
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87
$Pb^{4+} + 2e^- \rightleftharpoons Pb^{2+}$	+1.67
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$Ag^+ + 1e^- \rightleftharpoons Ag$	+0.80
$Fe^{3+} + 1e^- \rightleftharpoons Fe^{2+}$	+0.77
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	-0.13
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	-0.44
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	-0.76
$Al^{3+} + 3e^- \rightleftharpoons Al$	-1.66
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	-2.36
$Li^+ + 1e^- \rightleftharpoons Li$	-3.05

2

Comparison of reactivities of the metals.

- An electrode with a positive value has a higher reduction potential. Hence, it works strong **oxidizing agent (SOA)**.
- An electrode with a negative value has a higher oxidation potential. Hence, it works strong **Reducing agent (SRA)**.

examples

Zn (-0.76 V)	Cu (+0.34 V)
SRA	SOA

Ni (-0.25 V)	Ag (+0.80 V)
SRA	SOA

3

Calculation of the EMF of electro-chemical cell.

The emf associated with any redox reaction can be calculated.

$$E_{cell}^o = E_{cathode (reduction)}^o - E_{anode (oxidation)}^o$$

Adding EMF

For Eg:

- For a reaction, $2Ag^+ (aq) + Cd \rightarrow 2Ag + Cd^{2+}(aq)$
- The SRP of $Ag^+/Ag = 0.80 V$, $Cd^{2+}/Cd = -0.40 V$
- Using the formula,

$$E_{cell}^o = 0.80 - (-0.40)$$

- $E_{cell}^o = 1.20 V$

4

To predict the spontaneity of redox reaction

Any redox reaction would occur spontaneously if the free energy change (ΔG) is negative.

$$E_{cell}^o = E_{cathode (reduction)}^o - E_{anode (oxidation)}^o$$

ΔG^o ; is negative	Spontaneous reaction
ΔG^o ; is positive	Non-spontaneous reaction

- Spontaneous redox reaction
 - positive E^o (standard conditions)
 - positive E (non-standard conditions)
 - negative ΔG

- Non-spontaneous redox reactions:
 - negative E^o
 - negative E
 - positive ΔG

7)

CONCENTRATION CELL

- It is a galvanic cell in which electrical energy is produced by the transfer of substance from one electrode having higher concentrated solution to other electrode having lower concentrated solution.

- It is made up of two half cells having identical electrodes, identical electrolyte with change in concentrations.

- The two half cells are joined by a salt bridge or a semi permeable membrane.

- Concentration cells are of two types:

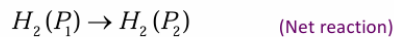
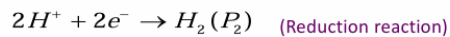
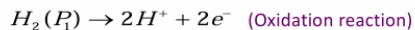
- Concentration cell without transfer
- Concentration cell with transfer

○ Concentration cell without transfer

▪ When two hydrogen electrodes of different gas pressures P_1 and P_2 ($P_1 > P_2$) are immersed in the same solution of hydrogen ions, oxidation of hydrogen takes place at left hand electrode and reduction of hydrogen takes place at right hand electrode.

▪ Cell representation: $\text{Pt}, \text{H}_2 (P_1) : \text{H}^+ || \text{H}^+ : \text{H}_2 (P_2), \text{Pt}$

Electrode reactions:



▪ From the above, there is no overall chemical change and there is only a transfer of hydrogen gas from the electrode with pressure P_1 , to the electrode with pressure P_2 .

▪ In this case, the emf of electrode depends only on the two pressures and is independent of the concentration of hydrogen ions in which electrodes are immersed.

$$E_{\text{cell}} = \frac{2.303RT}{2F} \log \frac{P_1}{P_2}$$

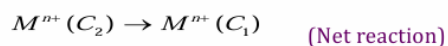
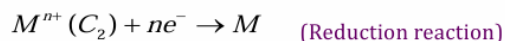
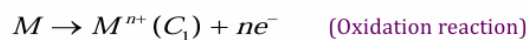
$$E_{\text{cell}} = \frac{0.059}{2} \log \frac{P_1}{P_2}$$

Concentration cell with transfer

▪ In this, electrodes are identical but electrolyte solution has different concentrations.

▪ Due to difference in the concentration of electrolyte there occurs corresponding change in the potential of the electrodes dipping in them.

▪ When the two electrodes of same metal (M) are dipped in of its own ion solution with different concentrations of C_1 and C_2 ($C_2 > C_1$) and connected with a salt bridge, the following reactions takes place:



➤ Cell representation: $\text{M} : \text{M}^{n+} (C_1) || \text{M}^{n+} (C_2) : \text{M}$

➤ Nernst equation for electrodes

$$E_{\text{right}} = E^o + \frac{0.059}{n} \log C_2 \quad E_{\text{left}} = E^o + \frac{0.059}{n} \log C_1$$

$$\therefore E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

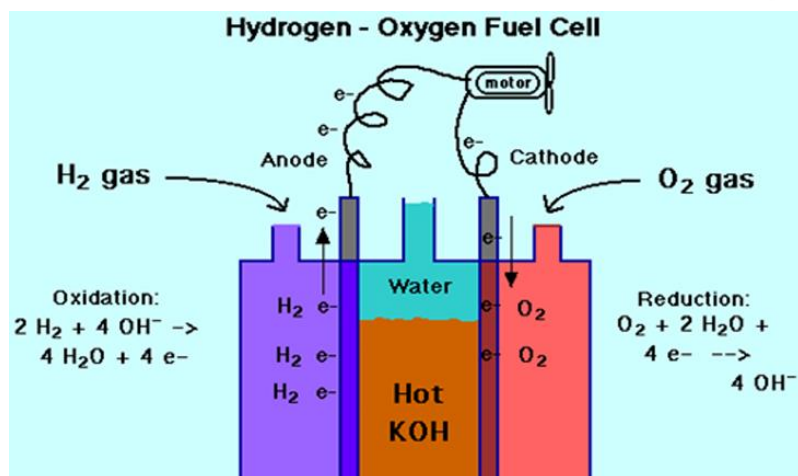
$$E_{\text{cell}} = \left[E^o + \frac{0.059}{n} \log C_2 \right] - \left[E^o + \frac{0.059}{n} \log C_1 \right]$$

$$E_{\text{cell}} = \frac{0.059}{n} \log \frac{C_2}{C_1}$$

8)
 εElectrode is made of graphite impregnated with fine powder of Pt or an alloy of Pb with Ag or Ni

3. Fuel Cell: A galvanic cell where there is a continuous supply of reactants.

It consists of two inert porous electrodes made of graphite impregnated with finely divided Pt and 25% KOH solution as electrolyte. Hydrogen gas is bubbled through one inert electrode, acts as anode. Oxygen gas is bubbled through another electrode, acts as cathode. The hydrogen-oxygen fuel cell produces water as a product and hence is an ideal power source for zero-emission vehicles. Hence it is called an eco friendly battery.



Redox Reaction in a Hydrogen- oxygen Fuel Cell

At Anode: $2 (H_2 (g) + 2OH^-(aq) \rightarrow 2 H_2O (l) + 2e^-)$ (Oxidation)

At Cathode: $O_2 (g) + 2 H_2O (l) + 4e^- \rightarrow 4OH^-(aq)$ (Reduction)

Net Reaction: $2 H_2 (g) + O_2 (g) \rightarrow 2 H_2O (l) + 1.0V$

Applications

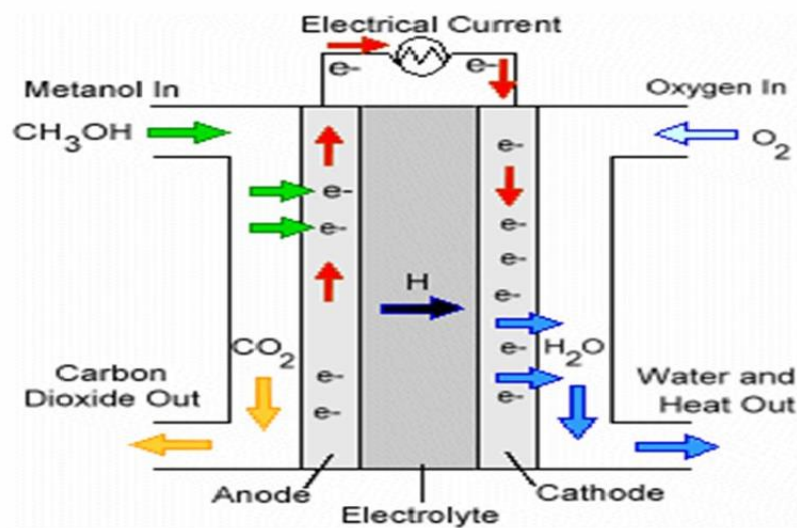
- ≈ They are used as auxiliary energy source in space vehicles, submarines etc.
- ≈ Because of light weight and pure drinking water formation, they are highly useful in space crafts.

Limitations

- ≈ Life time of fuel cells is not known accurately.
- ≈ Initial cost is high.
- ≈ The distribution of H_2 is not proper.

9)

Methyl alcohol oxygen fuel cell:



Methyl alcohol fuel cell

The reactions you're referring to seem to involve a fuel cell or electrochemical process, possibly for a methanol fuel cell or a similar system. Here's the correct representation of the reactions based on your input:

Anode Reaction (Methanol Oxidation):

At the anode, methanol (CH_3OH) is oxidized to carbon dioxide (CO_2), releasing protons (H^+) and electrons (e^-):



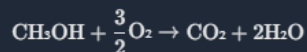
Cathode Reaction (Oxygen Reduction):

At the cathode, oxygen (O_2) is reduced by gaining protons (H^+) and electrons (e^-) to form water (H_2O):



Overall Reaction:

Combining the two half-reactions, we get the overall reaction for the fuel cell:



This overall reaction shows the oxidation of methanol to carbon dioxide and water, with the reduction of oxygen to water at the cathode. This type of reaction is typical in direct methanol fuel cells (DMFCs), which are used in various energy applications.

Limitations

- εMethanol toxic and flammable

- εProduce limited power

Advantages

- εStorage of methanol is easy

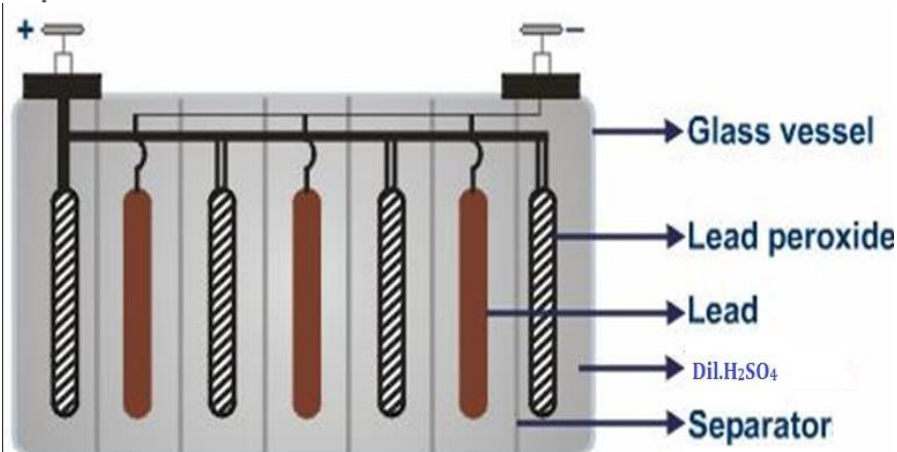
10)

Secondary Battery (Lead Acid and Nickel metal hydride)

Storage cell: it is the one which can act both as voltaic cell and electrolytic cell. When it functions as voltaic cell, it supplies electric current and the process is known as discharging. When it functions as electrolytic cell, it receives electric current and this process is known as charging. So it can be used for a large no. of cycles of charging and discharging. The best example for storage cell is lead acid battery or lead acid accumulator.

1. **Lead-acid battery:** Lead-acid is the oldest rechargeable battery in existence. Invented by the French physician Gaston Planté in 1859, lead-acid was the first rechargeable battery for commercial use. 150 years later, we still have no cost-effective alternatives for cars, wheelchairs, scooters, golf carts and UPS systems.

Construction: Large number of anodes and cathodes are arranged alternatively in a series separated by insulators as shown above. The entire set up is immersed in dilute sulphuric acid solution.



- εIt can act as voltaic cell and electrolytic cell.

- εEach cell has voltage 2 volts.

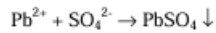
- εMany such cells connected in series develop total potential.

- εA 12V battery has six cells

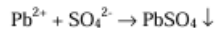
Discharging:

Reactions taking place during discharging: During discharging, it acts as voltaic cell and supplies electrical energy.

Anode: $\text{Pb} \rightarrow \text{Pb}^{2+} + 2\text{e}^-$ (oxidation)



Cathode: $\text{PbO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O}$ (Reduction)



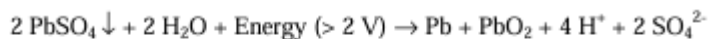
Net reaction: $\text{Pb} + \text{PbO}_2 + 4\text{H}^+ + 2\text{SO}_4^{2-} \rightarrow 2\text{PbSO}_4 \downarrow + 2\text{H}_2\text{O} + \text{Energy} (= 2\text{ V})$

The following points can be noticed from the above reaction:

- The concentration of sulphuric acid decreases in course of reaction.
- Both the electrodes are covered with lead sulphate.
- As lead sulphate is insoluble in sulphuric acid, it acts as a protective layer and prevents the further corrosion of lead.

As the lead sulphate deposited at both the electrodes is solid, the cell reactions can easily be reversed by passing emf just above the voltage of the cell i.e. $> 2\text{ V}$.

Charging:



Application: Car battery

11)

NiMH Principles of Operation

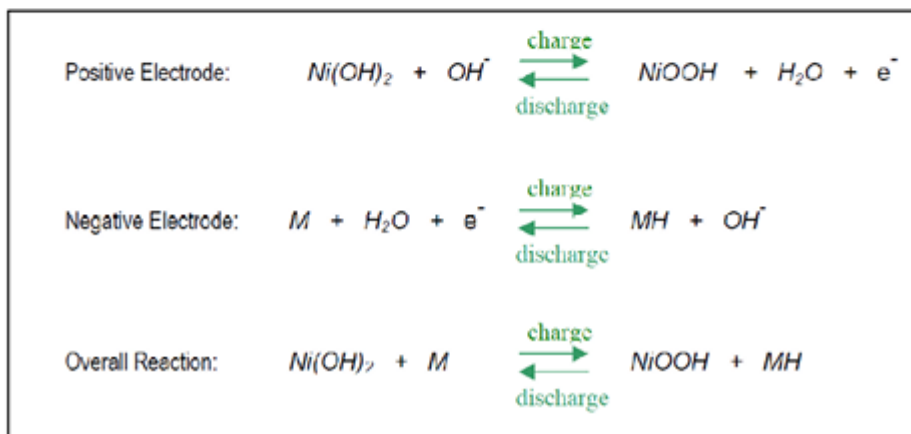
The principles in which NiMH cells operate are based on their ability to absorb, release, and transport (move) hydrogen between the electrodes within the cell. The following sections will discuss the chemical reactions occurring within the cell when charged and discharged and the adverse effects of overcharge and overdischarge conditions.

The success of the NiMH battery technology comes from the rare earth, hydrogen-absorbing alloys (commonly known as Misch metals) used in the negative electrode. These metal alloys contribute to the high energy density of the NiMH negative electrode that results in an increase in the volume available for the positive electrode. This is the primary reason for the higher capacity and longer service life of NiMH batteries over competing secondary batteries.

Charging Chemical Reaction

When a NiMH cell is charged, the positive electrode releases hydrogen into the electrolyte. The hydrogen in turn is absorbed and stored in the negative electrode. The reaction begins when the nickel hydroxide ($\text{Ni}(\text{OH})_2$) in the positive electrode and hydroxide (OH^-) from the electrolyte combine.

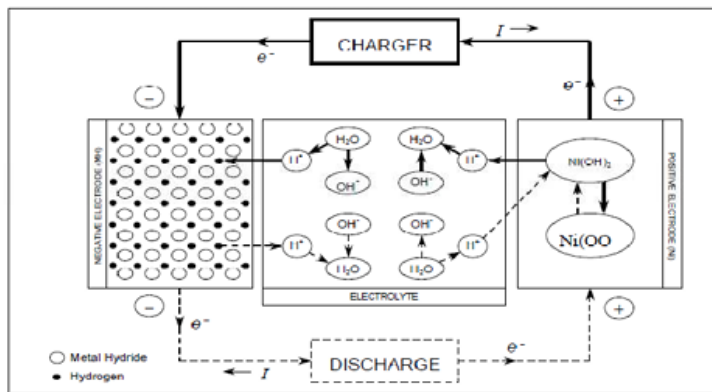
This produces nickel oxyhydroxide (NiOOH) within the positive electrode, water (H_2O) in the electrolyte, and one free electron (e^-). At the negative electrode the metal alloy (M) in the negative electrode, water (H_2O) from the electrolyte, and an electron (e^-) react to produce metal hydride (MH) in the negative electrode and hydroxide (OH^-) in the electrolyte.



NiMH cells are used in many applications, including:

- **Consumer electronics:** Digital cameras, remote controls, cordless phones, and more
- **Electric vehicles:** NiMH cells were used in first-generation electric vehicles
- **Medical devices:** Infusion pumps and portable diagnostic devices
- **Power tools:** Drills, saws, and screwdrivers

- **Solar energy storage:** NiMH batteries store electrical energy generated during the day for later use



12)

Lithium ion Battery

A lithium-ion battery (sometimes Li-ion battery or LIB) is a family of rechargeable battery types in which lithium ions move from the negative electrode to the positive electrode during discharge, and back when charging. Chemistry, performance, cost, and safety characteristics vary across LIB types. Unlike lithium primary batteries (which are disposable), lithium-ion electrochemical cells use an intercalated lithium compound as the electrode material instead of metallic lithium.

During discharge, lithium ions Li^+ carry the current from the negative to the positive electrode, through the non - aqueous electrolyte and separator diaphragm.

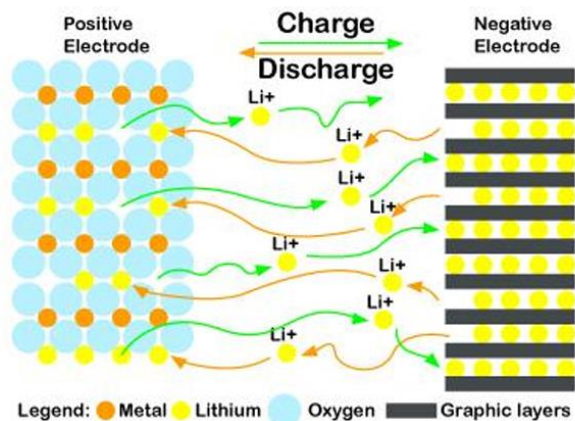
During charging, an external electrical power source (the charging circuit) applies a higher voltage (but of the same polarity) than that produced by the battery, forcing the current to pass in the reverse direction. The lithium ions then migrate from the positive to the negative electrode, where they become embedded in the porous electrode material in a process known as intercalation.

The three participants in the electrochemical reactions in a lithium-ion battery are the anode, cathode, and electrolyte.

Both the anode and cathode are materials into which, and from which, lithium can migrate. During insertion or intercalation lithium moves into the electrode. During the reverse process, extraction or deintercalation, lithium moves back out. When a lithium-based cell is discharging, the lithium is extracted from the anode and inserted into the cathode. When the cell is charging, the reverse occurs.

Lithium ion battery

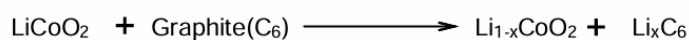
These batteries contain lithium ions instead of metallic lithium



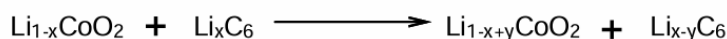
~ In these cells, oxidation and reduction reactions does not takes place

~ transport of Li^+ ions from one electrode to another electrode through the electrolyte

Charging Process



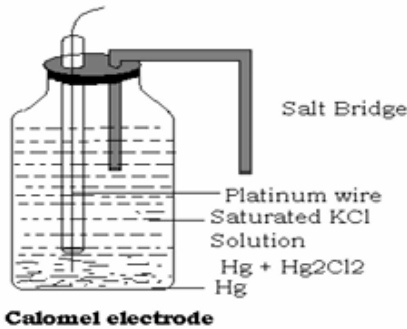
Discharging Process



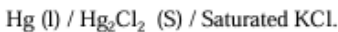
Example uses: ☐ Telecommunication ; PV Generation ; ☐ Wind Generator

☐ Power Tools ; E-bike ; ☐ Street Lighting System ; ☐ UPS and Backup System

13)
Construction and working of Calomel electrode



Calomel electrode consisting of a glass container at the bottom of which mercury is placed above which a layer of mercury and mercurous chloride (called calomel) is placed with 3/4th of bottle is filled with saturated KCl solution. Electrode potential of the cell depends on the concentration of KCl used. The calomel electrode can be represented as.



The calomel electrode acts as both anode and cathode depending upon the other electrode used. The platinum wire is used for electrical connections. Salt bridge is used to couple with other half cell.

When it acts as anode the electrode reactions is,



When it acts as cathode the electrode reaction is



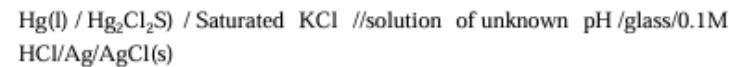
Advantages of Calomel Electrode: It is simple to construct.

The electrode potential is reproducible and stable. It is used as a reference electrode.

14)
Determination of pH using glass electrode.

To determine pH of **unknown solution** the glass electrode is combined with secondary reference electrode such as calomel electrode and the glass - calomel electrode assembly is dipped in the solution whose pH is to be determined. The two electrodes are connected to potentiometer or pH meter.

The combined electrodes can be represented as.



The emf of the above cell is given by

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

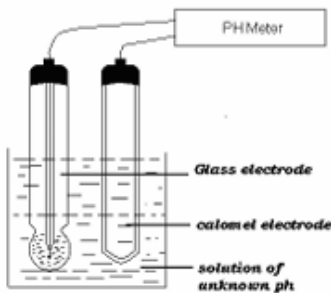
$$E_{\text{cell}} = E_{\text{calomel}} - E_{\text{glass}}$$

$$= E_{\text{SCE}} - E_{\text{G}}$$

$$= 0.2422 - (E^{\circ}_{\text{Glass}} - 0.0591 \text{ pH}) \qquad [E_{\text{G}} = E^{\circ}_{\text{G}} - 0.0591 \text{pH}]$$

$$E_{\text{cell}} = 0.2422 - E^{\circ}_{\text{G}} + 0.0591 \text{ pH}$$

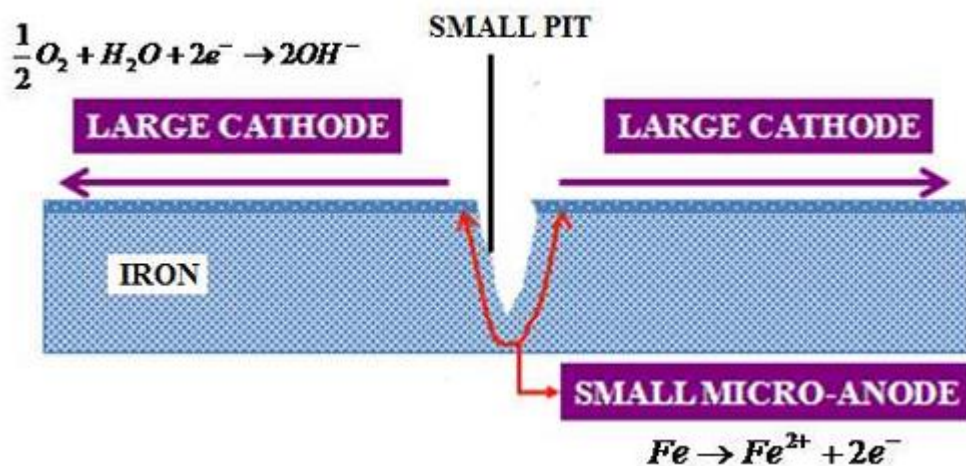
$$\text{pH} = \frac{E_{\text{cell}} + E^{\circ}_{\text{G}} - 0.2422}{0.0591}$$



15)

3. Pitting Corrosion:

- * Pitting of metal occurs where there is a break in the protective layer.
- * Pitting corrosion is a non uniform corrosion resulting from a localized accelerated attack and results in the formation of pits, cavities and pin holes in the metal.
- * This gives rise to the formation of small anodic and large cathodic areas.
- * The presence of the impurities (like sand, dust, scale etc) on the surfaces of metals also leads pitting.
- * A part below the impurity become the anodic area undergoes corrosion and the surrounding part become the cathodic area.
- * Once a small pit is formed, the rate of corrosion will be increased.



Causes:

- Damage/cracking of protective film over the metal.
- Materials having poor surface finish.
- Presence of impurities on metal surfaces (sand & dust).
- Stagnant water conditions favor pitting (low velocity)
- Chemical attack (Chloride damages the protective oxide layer).

Ways to prevent pitting corrosion :

- Selection of appropriate material;
- Controlling oxygen level
- Providing stirring of the electrolyte;
- Control of the electrolyte composition (PH, chloride ions);
- Corrosion inhibitors;
- Anodic & Cathodic protection;
- Corrosion protection coatings

16)

FACTORS INFLUENCING THE RATE OF CORROSION

1. Nature of The Metal And Its Surface

a. Position of metal in galvanic series:

- It determines the extent of corrosion.
- The metal higher in the electrochemical series acts anode which undergoes corrosion easily, the metals lower in the series acts as cathode which is protected from corrosion due to their higher oxidation potentials.
- The greater difference in their electrode potential faster is the rate of corrosion.

b. Over voltage:

- Over voltage decreases rate of corrosion increases.

c. Purity of the metal:

- The impure metals are prone to corrosion than the pure ones.
- Impurities cause heterogeneity and form tiny electrochemical cells where anodic part gets corroded.
- The effect of even traces of impurities on the rate of corrosion will be as follows.

Metal	% purity	Corrosion rate
Zinc	99.999	1
Zinc	99.99	2650
Zinc	99.95	5000

d. Surface of metal:

- A rough surface metal readily undergo corrosion due to collection of more dirt.
- A polished surface does not corrode easily.

e. Stressed part of a metal:

- Stress in metal surface is produced by mechanical operations such as welding bending, pressing etc.
- The portion subjected to more stress acts as anode and other portion acts as cathode.

f. Ratio of anodic area to cathodic area:

- The rate of corrosion increases with decrease in the ratio of anodic area to cathodic area.
- The smaller the ratio larger is the cathodic area and higher is the demand for electrons i.e. Rapid corrosion of small anodic area.
- For example, steel rivets (anode) are in copper sheets, steel rivets are completely corroded.

g. Physical state of the metal:

- ✓ The rate of corrosion is influenced by the physical state of a metal.
- ✓ For instance, the smaller the grain size of the metal or alloy, the greater will be the rate of corrosion.

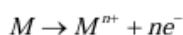
17)

2) Electrochemical Corrosion (or) Wet Corrosion

- ✦ This corrosion occurs due to the existence of separate anodic and cathodic parts, between which current flows through the conducting solution.
- ✦ At anodic area, oxidation reaction occurs, thereby destroying the anodic metal due to dissolution. Hence, corrosion always occurs at anodic parts.
- ✦ At cathodic area, reduction reaction occurs.
- ✦ These anodic and cathodic regions are formed due to several factors like
 - On a metal surface if the concentration of oxygen is different
 - Due to contact of two different metals
 - If metal surface is subjected to stress

Anodic Reaction:

- ✓ At anode oxidation takes place so that metal is converted into metal ions with the liberation of electrons.
- ✓ These electrons migrate towards cathode.



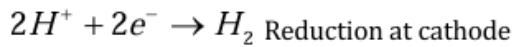
Cathodic Reaction:

- ✓ At cathode reduction takes place. Depending upon the nature of the corrosive environment cathodic reaction takes place in the following way:

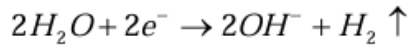
- Evolution of hydrogen.
- Absorption of oxygen depending upon the nature of corrosion environment.

a) Evolution of Hydrogen type:

- ★ In acidic medium and in the absence of oxygen, H^+ ions are reduced to H_2 gas.

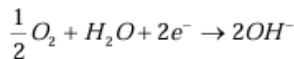


- ★ In basic medium and in the absence of oxygen, the cathodic reaction is,



b) Absorption of oxygen:

- ★ In neutral and aerated medium: If the solution is neutral and aerated, hydroxyl ions are formed as follows.



18)

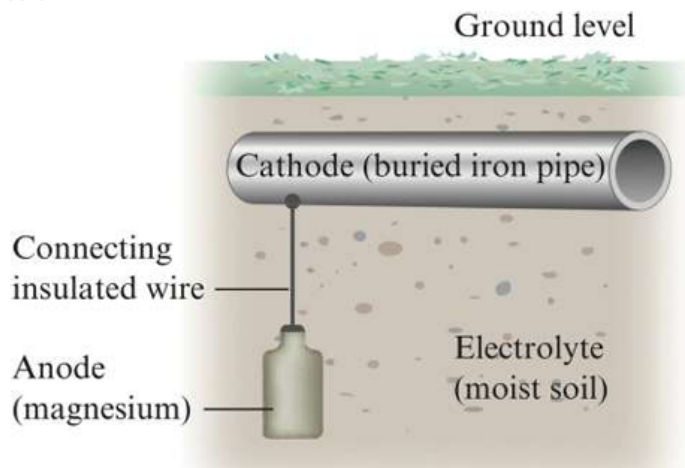
PROTECTION METHODS OF CORROSION

1. CATHODIC PROTECTION:

- ✦ The principle involved in this method is to force the metal to be protected to behave like a cathode, there by corrosion does not occur.
- ✦ There are two types of cathodic protection.

Sacrificial Anodic Protection Method:

- ♣ In this method, the metallic structure to be protected is connected by a wire to a more anodic metal.
- ♣ Thus during corrosion more anodic metal gets corroded while the parent metal is protected.
- ♣ The more active metal used is known as **sacrificial** anode which is replaced from time to time by fresh one.
- ♣ Metals commonly used as **sacrificial** anode are magnesium and zinc.
- ♣ This method is used for the protection of ships and boats. Sheets of zinc or magnesium are hung around the hull of the ship. Zinc and magnesium undergo corrosion.



Sacrificial anodic protection

Applications: Important applications of sacrificial anodic method include protection of buried lines, underground cables, marine structures etc

19)

CATHODIC PROTECTION :

♥ The principle involved in this method is to force the metal to be protected to behave like a cathode, there by corrosion does not occur.

♥ There are two types of cathodic protection.

a) Sacrificial Anodic Protection Method:

b) Impressed Current Cathodic Protection:

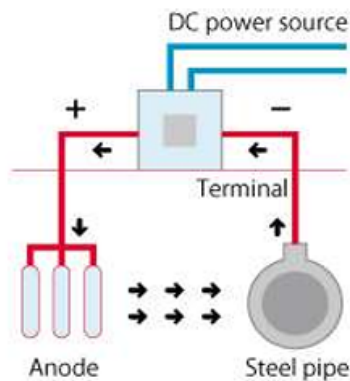
- ♣ In this method, the metallic object to be protected is made cathode by connecting it with the negative terminal of the DC source.
- ♣ The positive terminal is connected to an insoluble anode like graphite, scrap iron or platinum.
- ♣ The impressed current nullifies the corrosion current.
- ♣ The electrons flow to the metallic object as a result it acts as cathode and is protected.

Applications:

- ☞ These methods are used for the protection of buried pipelines, under ground cables, water tanks etc.

Problems and limitations:

- ✓ Capital investment and maintenance costs.
- ✓ Chemical reactions taking place at the surface of protected structure.
- ✓ Possibility of soil and microbiological corrosion.



Impressed current cathodic protection

Applications:

- Submarines are protected against corrosion by connecting the negative terminal of DC generators to the surface.
- Water tanks, buried oil or water pipelines, transmission line towers are protected by this method.

20)

The basic principles of electrochemical corrosion are:

- **Electrochemical cell**

Electrochemical corrosion requires an anode, a cathode, an electrolyte, and a flow of electricity between the anode and the cathode.

- **Anodic corrosion**

The anode corrodes preferentially over the cathode.

- **Corrosion rate**

The smaller the anode area relative to the cathode area, the faster the corrosion rate.

- **Corrosion rate calculation**

Corrosion rate can be calculated using Faraday's law, which expresses weight loss as a function of the metal's consumption rate, the current flow, and the time the metal is exposed to the current.

- **Electrochemical impedance spectroscopy (EIS)**

EIS is a method used to study corrosion systems. EIS can use small amplitude signals without significantly disturbing the properties being measured.

- **Polarization curves**

Polarization curves can be used to study the electrochemical corrosion behavior of metals and alloys.

.Wet Corrosion: or Electro Chemical Corrosion:

Wet corrosion of metals occurs through electron transfer, involving two processes, oxidation and reduction. In oxidation, the metal atoms lose electrons. The surrounding environment then gains the electrons in reduction. The metal, where electrons are lost, is called the anode. The other metal, liquid or gas which gains the electrons is called the cathode.

Eg: $\text{Fe} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_2$

Mechanism:

At Anode: Oxidation occurs $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$

At Cathode: Reduction occurs and it depends on nature of the environment

Acidic environment:

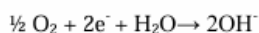
Hydrogen evolution: All metals above H_2 in electrochemical series undergo this type of corrosion

Example: Iron metal in contact with HCl .

($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$)

Neutral or basic environment:

Absorption of oxygen: or Formation of hydroxide ion type corrosion.



Example: Iron metal in contact with a neutral solution.

Net Corrosion is $\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe}(\text{OH})_2 \rightarrow \text{Fe}(\text{OH})_3 \rightarrow [\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}]$ Rust

An example of wet corrosion is copper fitting on a steel pipe carrying water. Steel pipe acts as the anode, copper fitting, the cathode. The pipe is in direct contact with the fitting for the connection.

Water acts as electrolyte, allowing for migration of the ions, and completion of the circuit.

22)

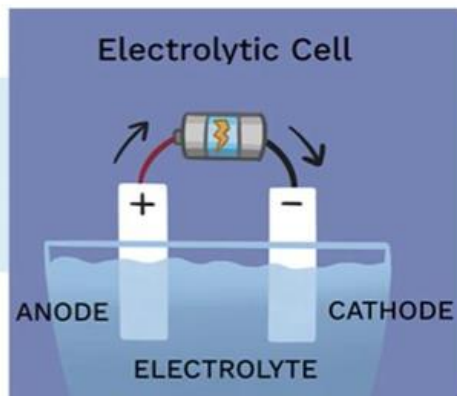
Electroplating

Electroplating:

Coating of coat metal on the surface of base metal by passing a direct current through an electrolytic solution is called electroplating.

At Anode: Oxidation takes place
(loosing of electrons)

At Cathode: Reduction take place
(gaining of electrons)



Electro plating is the process of deposition of a metal, nonmetal or alloy by passing electric current through an electrolytic solution containing soluble salt of the coating metal.

The process of electroplating consists of two steps

- Surface preparation
- Electro deposition

1) Surface preparation

1) Mechanical Cleaning:

- The metal surface is cleaned mechanically with brushes, knives, cutters, chisels, then heated and washed.

2) Alkali cleaning:

- ✓ Alkaline solution of sodium hydroxide, sodium carbonate, etc., removes oils, greases and impurities.

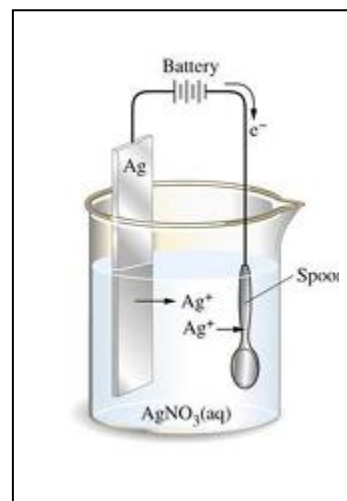
3) Solvent Cleaning:

- ✓ Oils, Fatty substances and greases are removed by Solvents wash (CCl_4 , & acetone)
- ✓ metal surface is washed with hot water

1) Electro-deposition:

Electroplating With Gold:

- Cathode: Article to be electroplated (Spoon)
- Anode: Block of gold metal
- Electrolyte: Aqueous solution of AuCl_3 or Potassium auro-cyanide $\text{K}[\text{Au}(\text{CN})_2]$
- Process: Gold metal act as anode undergo dissolution, get deposited on the cathode (spoon) by passing electricity.



23)

Anodic coating		Cathodic Coating
This type of coating protect base metal sacrificially.	1	This type of coating protect the base metal because of high corrosion resistance and noble behaviour
The coating metal is at lower electrode potential than base metal.	2	The coating metal is at higher electrode potential than base metal.
Corrosion of base metal does not enhance even on breaking "anodic coating" as it heals its film	3	Corrosion of base metal enhances, if there is a small cut in coating
Eg. Galvanising i.e. Zn coating on iron/steel	4	Eg. Tinning i.e. tin coating on iron/steel/copper/brass.

It protects the base metal sacrificially due to more electropositive character of the coating metal.	It protects the base metal due to high corrosion resistance & noble behavior of the coating metal.
Coating metal is at lower potential than the base metal.	Coating metal is at higher potential than the base metal.
Corrosion of base metal does not increase even on breaking of the coating as it heals its film.	Corrosion of base metal increases, if there is a break in the coating.
Galvanizing i.e. coating of Zn coating iron/steel is an example of anodic coating.	Tinning i.e. coating of Sn coating iron/steel is an example of cathodic coating.

THEORIES (OR) MECHANISM OF CORROSION

There are Two theories of corrosion

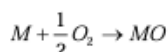
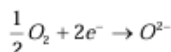
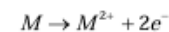
- * Dry or Chemical Corrosion
- * Wet or Electrochemical Corrosion

1) Direct Chemical Attack (Or) Mechanism Of Dry Corrosion

- ◆ The direct chemical action of atmosphere gases like oxygen, halogen, H₂S etc in a dry environment on metals, a solid film of the corrosion product is formed on the surface of the metal.
- ◆ This is known as chemical corrosion.

a. Oxidation Corrosion (Reaction With Oxygen)

- ★ Some of the metals directly react with oxygen in the absence of moisture.
- ★ Then the metal gets oxidized to metal ions and the electrons so released reduce oxygen to form oxide ion.
- ★ The metal ion and oxide ion combine to form metal oxide on the metal surface.



- ★ The nature of metal oxide layer formed plays an important role in determining further corrosion.

1) Protective and non porous oxide film: Metals such as Al, Cr, Cu & W develop nonporous, stable oxide film on the surface. This film prevents further corrosion of the metal.

2) Unstable oxide film: Au & Pt develop unstable oxide film which instantaneously decomposes to form metal & oxygen.

3) Volatile oxide film: Molybdenum develops an oxide which immediately vaporizes. As a result metal surface easily undergoes further corrosion.

4) Porous and non protective film: Alkali and alkaline earth metals form porous oxide layer which further facilitates corrosion of the metal due to porous nature. Oxide layer cannot protect the metal from corrosion.

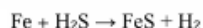
Pilling Bedworth rule: The protective or non protective nature of oxide film is determined by this rule. The ratio of volume of oxide film to the volume of metal consumed is known as Pilling-Bedworth rule.

- ★ If the ratio is <1, the metal oxide layer is porous and non protective. Ex:-Oxide layer on alkaline metals
- ★ If the ratio is ≥1, the metal oxide layer is non porous protective layer. It stops further corrosion of metal. Ex:-Oxide layer on Al, Cr, Cu, W.

$$\text{Pilling Bedworth rule} = \frac{\text{Vol. of metal oxide layer}}{\text{Vol of metal consumed}}$$

b. Corrosion By Other Gases:

- ✦ This type of corrosion is due to the attack of other gases like Cl₂, SO₂, H₂S, NO_x in dry atmosphere on the metal.
- ✦ The corrosion products may be protective or non-protective.
- ✦ Dry Cl₂ reacts with Ag and forms AgCl which is protective layer, Eg: 2 Ag + Cl₂ → 2AgCl (protective),
- ✦ where as SnCl₄ is volatile, Sn + 2Cl₂ = SnCl₄
- ✦ H₂ Embrittlement: Formation of cracks and blisters on metal surface due to high pressure of H₂ gas.



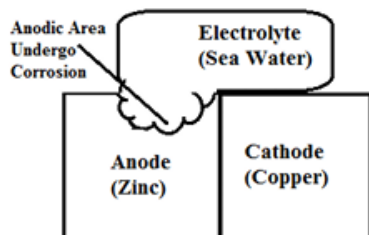
c. Liquid Metal Corrosion:

- * This type of corrosion takes place, when molten metal passes through metallic pipes due to dissolution of solid metal by liquid molten metal or due to internal penetration of solid metal into liquid metal.
- * For example: Liquid metal mercury dissolves most metals by forming amalgams, thereby corroding them.
- * Coolant (sodium metal) leads to corrosion of cadmium (moderator) in nuclear reactors.

25)

1. Galvanic Corrosion:

- When two dissimilar metals are connected in presence of a corrosive environment, then the metal higher in electrochemical series undergoes corrosion.
- This type of corrosion is also called galvanic corrosion or bimetallic corrosion.
- For example, zinc and copper constitute a galvanic couple, where zinc acts as anode and undergo corrosion and copper behaves as cathode and get protected from corrosion.
- The extent of corrosion depends on the potential difference between the two metals.
- This galvanic corrosion can be minimized by
 - Avoiding galvanic couple
 - Selecting metals closely placed in electrochemical series as galvanic couple
 - Providing an insulating material between the two metals



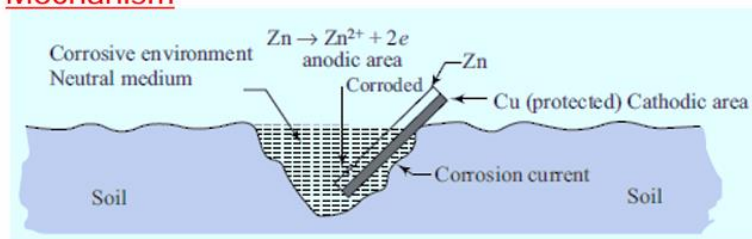
Requires three conditions:

Dissimilar metals must be present.

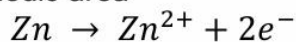
Metals must be in electrical contact.

Metals must be exposed to an electrolyte.

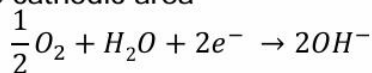
Mechanism



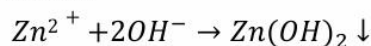
In the anodic area



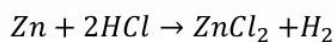
In the cathodic area



Overall



In an acid medium



Factors of Galvanic Corrosion

- Difference between the electrode potentials of the two metals.
 - A greater difference equals a stronger corrosion force.
- Contact resistance at the boundary between the two metals.
 - Corrosion is decreased due to high contact resistance.
- Electric resistance of electrolyte solution.
 - Solution dilution provides low corrosion rate.
- Anode-to-cathode areas ratio.
 - Low corrosion due to large area difference.
- Presence of passive film.
- Electrolyte solution properties
 - pH, oxygen content, temperature and flow rate.

Ways to prevent galvanic corrosion

- Materials with **similar corrosion** potentials should be selected.
- Electrical connection can be broken if the two metals are **insulated** from each other.
- The protective **coating** should be applied to both materials.
- The two materials should be **separated by inserting** a suitably sized spacer.
- A **sacrificial anode** should be installed, which is anodic to both the metals.
- A corrosion **inhibitor** can be added to the environment.

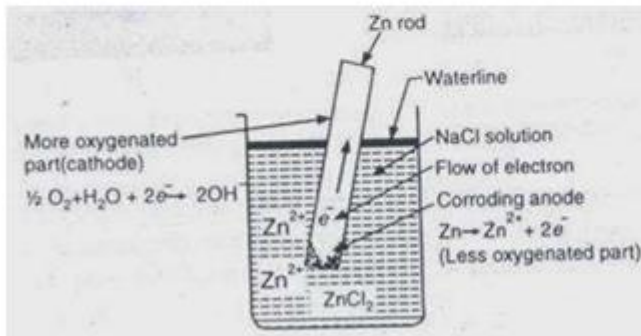
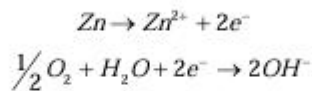
26)

Concentration Cell Corrosion (Differential Aeration Corrosion)

- This type of corrosion arises due to exposure of metal to varying concentration of electrolyte or of varying aeration.
- Differential aeration corrosion occurs when one part of metal is exposed to a different air concentration from the other part.
- Then, part of the metal exposed to **less concentration of oxygen acts as anode** and other parts exposed to **high concentration of oxygen act as cathodes**.
- Anodic part undergoes corrosion.
- Differential aeration accounts for the corrosion of metals, partially immersed in a solution, just below the waterline.

Example:

- If a metal is partially immersed in a dilute solution of a neutral salt solution, then the parts above the solution are more strongly aerated hence, become cathodic.
- If a metal part immersed to greater depth show a smaller oxygen concentration and thus become anodic.



amples: Water line corrosion, Drop corrosion

Similarly in case of Zn metal

Reaction at anode:- $\text{Zn(s)} \rightarrow \text{Zn}^{2+} + 2e^-$ (Oxidation)

Reaction at cathode:- $\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^-$ (Reduction)

Overall Reaction:- $\text{Zn} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2$ Or $2\text{Zn} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Zn(OH)}_2$

Ways to prevent differential aeration corrosion

- Using metallic coating, electroless plating or chemical conversion methods.
- Maintaining the materials own protective film.
- Controlling the chemistry of fluids and using inhibitors.