



**PES**  
UNIVERSITY

CELEBRATING 60 YEARS

## ENGINEERING CHEMISTRY

---

**Lata Pasupulety**

Department of Science and Humanities

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

---



### *Module content:*

- *Electrode potential and cell potential*
  - *Nernst Equation*
- *Types of electrodes*
- *Reference electrodes*
- *Concentration cells*
- *Ion-selective electrodes*

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

---



### *Class content:*

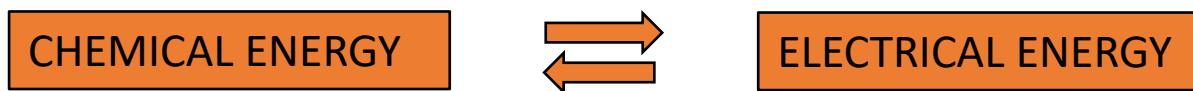
- *Origin of electrode potential*
- *Cell potential*
- *Nernst Equation*

# ENGINEERING CHEMISTRY

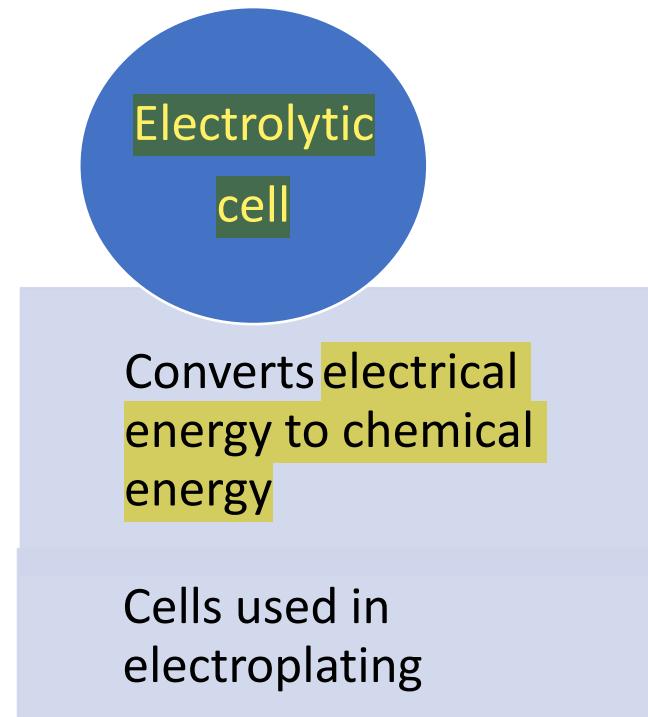
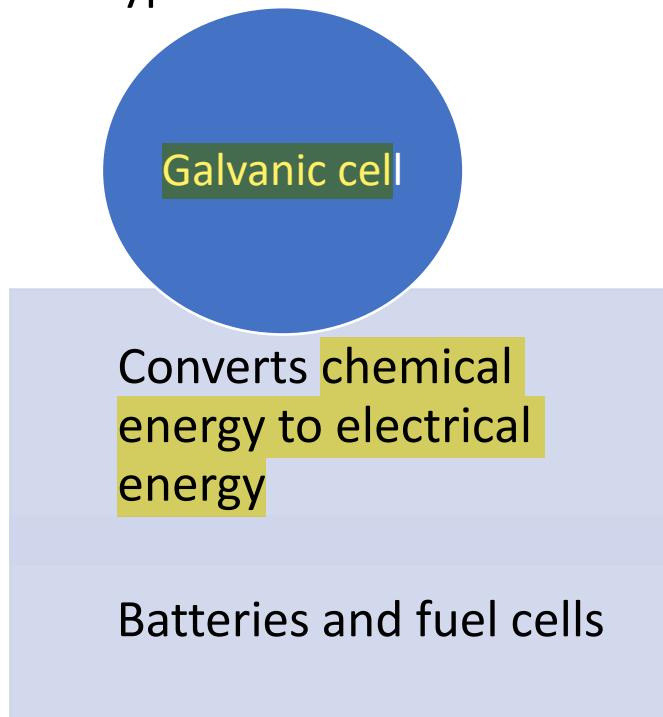
## Module 1- Electrochemical equilibria

### Electrochemistry

- Deals with the inter conversion of chemical energy and electrical energy



- Two types of cells:



# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

---

### Electrochemical studies:

- Redox reaction
- Electrodes- Anode (oxidation)  $\rightarrow \text{An}^{\text{Ox}}$   
Cathode (reduction)  $\rightarrow \text{RED CAT}$
- Electrolytic conductance through electrolyte due to movement of ions

Acid, alkali or salt solutions

Molten electrolytes

Solid electrolytes

### Electrode potential

- When a metal rod is dipped in a solution of its own ions, the electrical potential developed at the interface of the metal and its solution
- It is denoted by E

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

---

### Origin of Electrode potential

When a metal M is in contact with solution containing its ions

$M^{n+}$ , two reactions are possible:

#### 1. Ionisation (Oxidation)



#### 2. Deposition (Reduction)

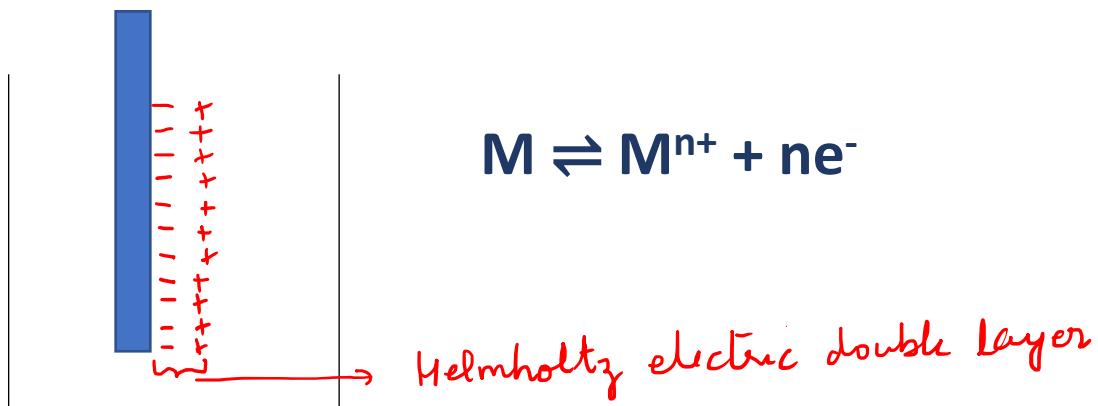


# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

### ➤ Case I : If ionization is faster than deposition

- the metal acquires net negative charge, consequently retards the rate of ionization and increases the rate of deposition. This ultimately lead to the establishment of equilibrium
- the metal electrode gets negatively charged and attracts the layer of positive ions at the interface
- an electrical double layer is formed at the interface of metal and solution known as **Helmholtz electrical double layer**

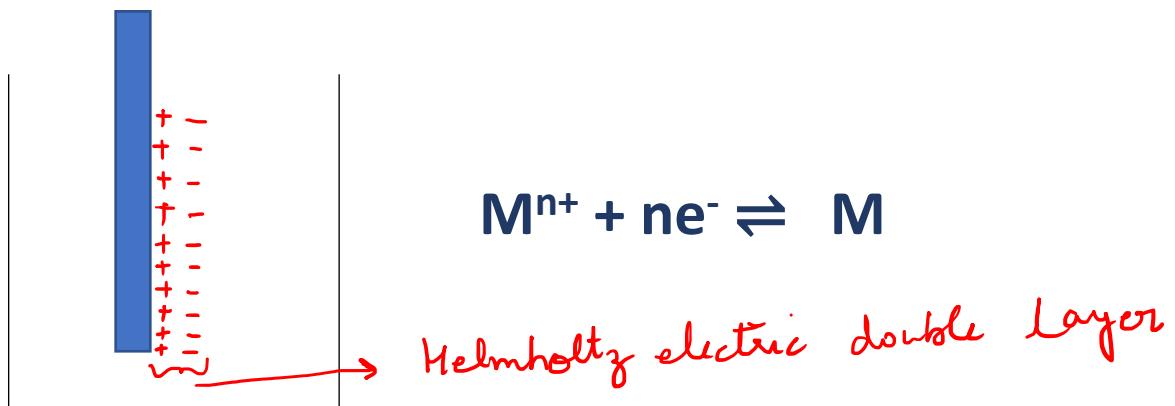


# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

### ➤ Case II : deposition is faster than ionization

- the metal acquires net positive charge, consequently retards the rate of deposition and increases rate of ionization. This ultimately lead to the establishment of equilibrium.
- The metal electrode gets positively charged and attracts the layer of negative ions at the interface,
- an electrical double layer is formed at the interface of metal and solution known as **Helmholtz electrical double layer**



# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

### Standard electrode potential

- The potential developed at the interface of metal and solution, when the metal is in contact with a solution of its own ions having unit concentration at 298 K
- In case of gas electrodes the partial pressure of gas is maintained at 1 atmospheric pressure.
- It is represented as  $E^\circ$

### Electrochemical Cell

Single electrode potentials cannot be measured hence two electrodes are coupled together to form a cell

### Cell notation

e.g. Daniel cell:



# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

### Cell potential

- The difference in electrode potentials of the electrodes constituting the cell
- It is denoted by  $E_{cell}$

### Standard cell potential

- $E_{cell}$  depends on concentration of the ions in the cell, temperature and the partial pressures of any gases involved in the cell reaction.
- When all the concentrations are 1M, all partial pressures of gases are 1atm and temperature is 298K, the emf is called Standard cell potential,  $E^o_{cell}$

### Calculation of $E_{cell}$

$$E_{cell} = E_{rhs} - E_{lhs} = E_{cathode} - E_{anode}$$

- $E_{cell}$  represents the driving force for the cell reaction to take place

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

- If reaction is spontaneous  $\Delta G$  is negative, thus  $E_{CELL}$  should be positive
- If reaction is non spontaneous  $\Delta G$  is positive, thus  $E_{CELL}$  should be negative

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

### Electrochemical Series:

- In order to predict the electrochemical behavior of an electrode – electrolyte system, elements are arranged in the order of their standard reduction potentials.
- This arrangement is known as electrochemical series.
- A negative value indicates oxidation tendency while a positive value indicates a reduction tendency.

### Electrochemical series

Equilibrium (Oxidants $\leftrightarrow$ Reductants)	E° (volts)
Lithium: $\text{Li}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Li}(\text{s})$	-3.03
Potassium: $\text{K}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{K}(\text{s})$	-2.92
Calcium: $\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Ca}(\text{s})$	-2.87
Sodium: $\text{Na}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Na}(\text{s})$	-2.71
Magnesium: $\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Mg}(\text{s})$	-2.37
Aluminum: $\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \leftrightarrow \text{Al}(\text{s})$	-1.66
Zinc: $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Zn}(\text{s})$	-0.76
Iron: $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Fe}(\text{s})$	-0.44
Lead: $\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Pb}(\text{s})$	-0.13
Hydrogen: $2\text{H}^+(\text{aq}) + 2\text{e}^- \leftrightarrow \text{H}_2(\text{g})$	0.00
Copper: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Cu}(\text{s})$	+0.34
Silver: $\text{Ag}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Ag}(\text{s})$	+0.80
Gold: $\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \leftrightarrow \text{Au}(\text{s})$	+1.50

Metal Reducing Activity Increasing  


Source:<https://www.syedgilanis.com/2019/04/electrochemicalseries.html>

Metal Oxidizing Activity Increasing  


# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

### Nernst equation for a single electrode

A quantitative relationship between electrode potential and concentration of species with which the electrode is reversible

The reaction at the electrode is



$$1F = 96500 \text{ C/mol}$$

The maximum work that can be obtained is

$$-\Delta G = W_{\max}$$

For an electrochemical system, maximum work done is

$$W_{\max} = \text{Total charge available} \times \text{Energy available per unit charge}$$

- **Total charge available**, i.e., No. of moles of electrons exchanged in redox reaction ( $n$ ) multiplied by charge carried per mole of electrons , $F(96,500 \text{ C/mol}) = nF$
- **Energy available per unit charge**, i.e., electrode potential because

$$\text{electrode potential} = \text{energy/unit charge} = E$$

$$\text{Therefore , } W_{\max} = nFE ; \Delta G = -nFE$$

$$\text{Under standard conditions, } \Delta G^\circ = -nFE^\circ$$

Decivation + Numerical

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria



A thermodynamic equation which relates reaction quotient and decrease in free energy is given by,

$$\Delta G = \Delta G^\circ + RT \ln Q, \text{ where } Q \text{ is the reaction quotient}$$

The reaction quotient for the reaction is,  $Q = [M]/[M^{n+}]$

Substituting for  $\Delta G$ ,  $\Delta G^\circ$  and  $Q$ , we get

$$-nFE = -nFE^\circ + RT \ln\left(\frac{[M]}{[M^{n+}]}\right)$$

Where,  $E^\circ$  = Standard electrode potential,  $n$  = number of electrons exchanged in the redox reaction,  $R$  = Gas constant.  $8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ,  $T$  = temp in Kelvin,  
 $F$  = Faraday  $96500 \text{ C mol}^{-1}$

dividing throughout by  $-nF$ ,  $E = E^\circ - \frac{RT}{nF} \ln\left(\frac{[M]}{[M^{n+}]}\right)$

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

since  $[M] = 1$  for pure substances, *and solids*

$$E = E^\circ + \frac{RT}{nF} \ln([M^{n+}]) \quad -\textcircled{1}$$

at 298K,

$$E = E^\circ + \frac{0.0591}{n} \log([M^{n+}]) \quad \rightarrow \quad \frac{8.314 \times 298}{96500} = 0.0591$$

Nernst equation may also be used to calculate. emf of electrochemical cells. For the cell reaction



$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Nernst equation is

$$E = E^\circ - \frac{0.0591}{n} \log \left( \frac{[C]^c [D]^d}{[A]^a [B]^b} \right)$$

$$E = E^\circ - \frac{2.303 \times R T}{n F} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$n$  = no. of e<sup>-</sup>s transferred,  $E^\circ_{cell}$  = std. emf of the cell



**THANK YOU**

---

**Lata Pasupulety**

Department of Science and Humanities

**latapasupulety@pes.edu**

+91 80 6666 3333 Extn 759



**PES**

UNIVERSITY

CELEBRATING 50 YEARS

# ENGINEERING CHEMISTRY

---

**Lata Pasupulety**

Department of Science and Humanities

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

---



### *Class content:*

- *Types of electrodes*
  - *Metal-metal-ion electrode*
  - *Metal-insoluble salt –ion electrode*
  - *Gas electrode*
  - *Amalgam electrode*
  - *Redox electrode*
  - *Ion selective electrode*

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

### Types of electrodes

- In order to form a cell, 2 half cells or 2 electrodes are required
- Various types of electrodes are available which are constructed based on the application

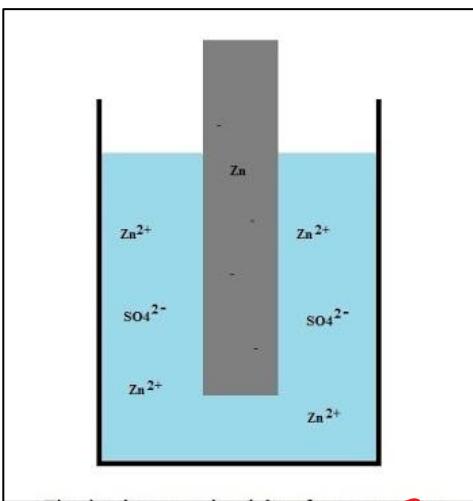
#### 1. Metal-metal ion electrode:

- Metal in contact with a solution of its own ions

e.g., Zn/Zn<sup>2+</sup>, Cu/Cu<sup>2+</sup>, Ag/Ag<sup>+</sup>

- $M^{n+} + ne^- \rightleftharpoons M$
- Nernst equation

$$E_{M/M^{n+}} = E_{M/M^{n+}}^{\circ} + \frac{2.303RT}{nF} \log [M^{n+}] \rightarrow [M] = 1$$



Source:[http://www.valgetal.com/physics/  
Batteries/batteries.htm](http://www.valgetal.com/physics/Batteries/batteries.htm)

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

### 2. Metal-Metal insoluble salt- ion electrode:

- These electrodes consist of a metal in contact with a sparingly soluble salt of the same metal dipped in a solution of soluble salt of the same anion

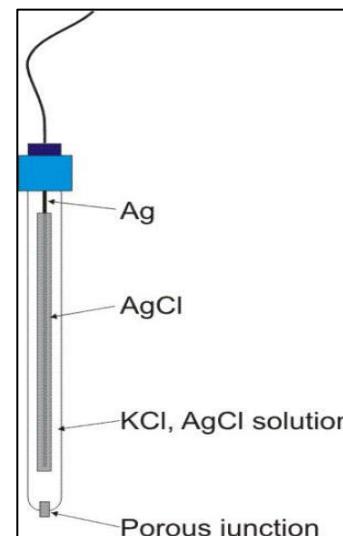
e.g., Calomel electrode  $\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{KCl}$ ,  $\text{Ag}/\text{AgCl}(\text{s})/\text{HCl}$

- For silver –silver chloride electrode



- Nernst equation:

$$E_{\text{Ag}/\text{AgCl}/\text{Cl}^-} = E^o_{\text{Ag}/\text{AgCl}/\text{Cl}^-} - \frac{0.0591}{1} \log[\text{Cl}^-]$$



Source:<https://www.corrosion-doctors.org/Corrosion-Thermodynamics/Reference-Half-Cells-Silver.htm>

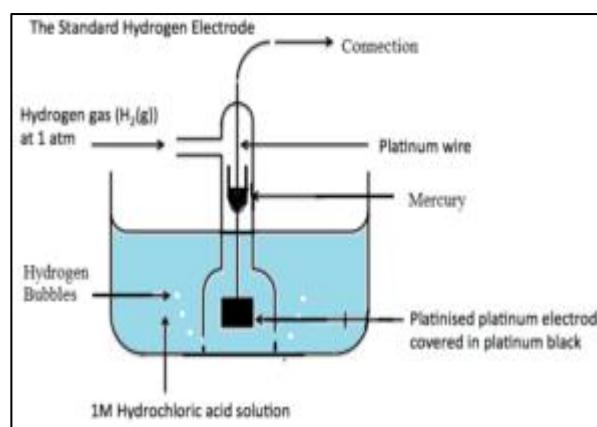
# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

### 3. Gas electrode:

- It consists of gas bubbling about an inert metal foil, immersed in solution containing ions to which the gas is reversible.
- The metal provides electrical contact and facilitates the establishment of equilibrium between the gas and its ions  
e.g., Hydrogen electrode Pt/H<sub>2</sub>/H<sup>+</sup>, Chlorine electrode Pt/Cl<sub>2</sub>/Cl<sup>-</sup>
- For a hydrogen electrode  
$$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$$
- Nernst equation:

$$E_{\text{Pt}/\text{H}_2/\text{H}^+} = E^0_{\text{Pt}/\text{H}_2/\text{H}^+} - \frac{0.0591}{2} \log\left(\frac{p_{\text{H}_2}}{[\text{H}^+]^2}\right)$$



Source:[https://thefactfactor.com/facts/pure\\_science/chemistry/physical-chemistry/reference-electrodes/5844/](https://thefactfactor.com/facts/pure_science/chemistry/physical-chemistry/reference-electrodes/5844/)

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

### 4. Amalgam electrode:

- It is similar to metal- metal ion electrode in which metal amalgam is in contact with a solution containing its own ions

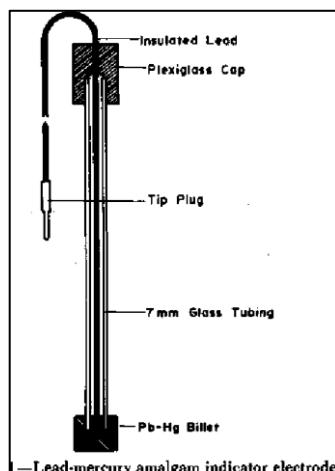
e.g., Lead amalgam electrode Pb-Hg/Pb<sup>2+</sup>

- For lead amalgam electrode



- Nernst equation:

$$E_{\text{Pb}^{2+}/\text{Pb-Hg}} = E^0_{\text{Pb}^{2+}/\text{Pb-Hg}} - \frac{0.0591}{2} \log\left(\frac{[\text{Pb-Hg}]}{[\text{Pb}^{2+}]}\right)$$



Source:<https://www.semanticscholar.org/paper/Potentiometric-Titration-of-Sulfate-in-Water-and-a-Robbins-Carter/c823ab0578481e876975ee707a5f8adca14c512f>

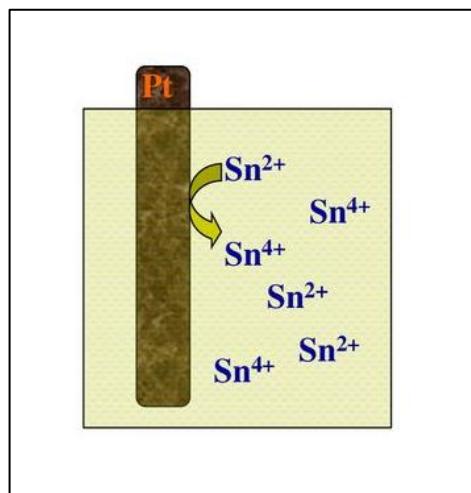
# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

### 5. Oxidation - reduction electrode :

- It consists of an inert metal such as platinum immersed in a solution containing an appropriate oxidized and reduced form of redox system.
- The metal merely acts as electrical contact.
- The potential arises due to the tendency of one form to change in to other form.  
e.g., Pt/Fe<sup>2+</sup>,Fe<sup>3+</sup>, Pt/Ce<sup>3+</sup>,Ce<sup>4+</sup> , Pt/Sn<sup>2+</sup>,Sn<sup>4+</sup>
- For stannous stannic electrode  
 $\text{Sn}^{4+} + 2\text{e}^- \rightleftharpoons \text{Sn}^{2+}$
- Nernst equation:

$$E_{\text{Pt}/\text{Sn}^{4+}/\text{Sn}^{2+}} = E^0_{\text{Pt}/\text{Sn}^{4+}/\text{Sn}^{2+}} - \frac{0.0591}{2} \log\left(\frac{[\text{Sn}^{2+}]}{[\text{Sn}^{4+}]}\right)$$



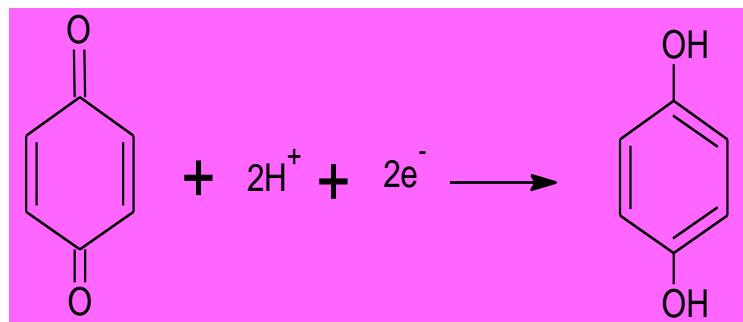
Source:<https://slideplayer.com/slide/13860805/>

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

### Quinhydrone electrode

- It consists of an inert metal such as platinum immersed in a solution containing quinone and hydroquinone
- The metal merely acts as electrical contact
- The potential arises due to the tendency of quinone to change to hydroquinone
- Pt/Q,QH<sub>2</sub>



• Nernst equation:  $E_{Pt/Q/QH_2} = E^o_{Pt/Q/QH_2} - \frac{0.0591}{2} \log\left(\frac{[QH_2]}{[Q][H^+]^2}\right)$

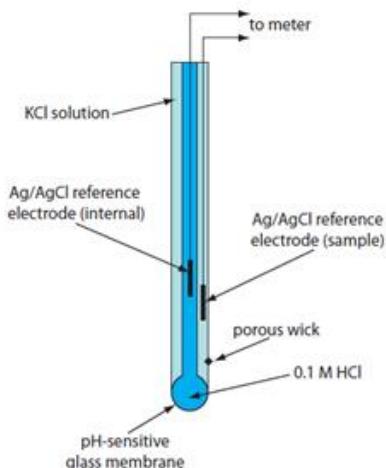
# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

### 6. Ion selective electrode:(membrane electrode)

- It consists of a membrane in contact with a solution, with which it can exchange ions.  
e.g., **glass electrode**: selective to  $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  etc.
- Equation for determining potential for pH sensitive Glass electrode

$$E_G = E_G^0 + 0.0591 \log_{10} [\text{H}^+]$$



Source:Analytical Chemistry 2.0, David Harvey,  
[community.asdlib.org/activelearning-textbook/](http://community.asdlib.org/activelearning-textbook/)



**PES**

UNIVERSITY

CELEBRATING 60 YEARS

**THANK YOU**

---

**Lata Pasupulety**

Department of Science and Humanities

**latapasupulety@pes.edu**

+91 80 6666 3333 Extn 759



**PES**  
UNIVERSITY  
CELEBRATING 60 YEARS

# ENGINEERING CHEMISTRY

---

**Lata Pasupulety**

Department of Science and Humanities

# ENGINEERING CHEMISTRY

## Module 4- Electrochemical equilibria

---



### *Class content:*

- *Reference electrodes*
  - *Primary reference electrode*
    - *Standard Hydrogen electrode*
  - *Secondary reference electrodes*
    - *Calomel electrode*
    - *Silver – silver chloride electrode*

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

---



### Reference electrodes

- Electrodes whose potentials are accurately known, stable and with reference to which the electrode potential of any electrode can be measured
- Reference electrode is combined with indicator electrode and emf of the cell is measured
- Two types of reference electrodes:
  - **Primary reference electrodes**
    - Standard Hydrogen electrode(SHE)
  - **Secondary reference electrodes**
    - Calomel electrode
    - Silver-silver chloride electrode

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

**Primary reference electrode:** Standard hydrogen electrode

- Electrode potential is assigned a value of  $0.0 \text{ V} \rightarrow \text{arbitrary}$
- Gas electrode
- $\text{Pt}/\text{H}_2/\text{H}^+$
- $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$
- Used to measure potential of other electrodes

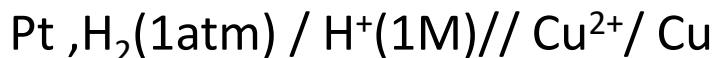
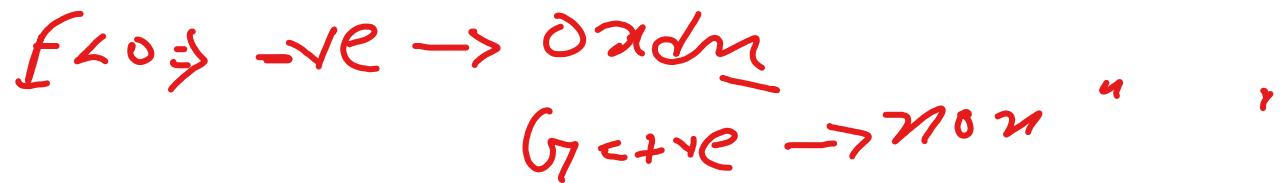
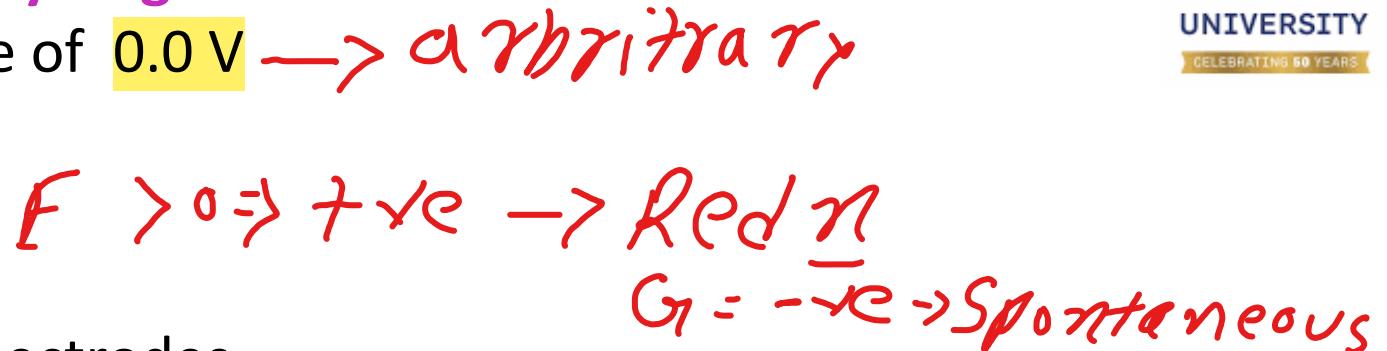
e.g.,



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

$$0.76 = 0.0 - E_{\text{Zn/Zn}^{2+}}$$

$$E_{\text{Zn/Zn}^{2+}} = -0.76 \text{ V}$$



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

$$0.34 = E_{\text{Cu/Cu}^{2+}} - 0.0$$

$$E_{\text{Cu/Cu}^{2+}} = 0.34 \text{ V}$$

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

---



### Disadvantages of SHE:

- Maintaining concentration of  $H^+$  ions at 1M and pressure of  $H_2$  gas at 1 atm is difficult.
- Platinum is highly susceptible to poisoning by different impurities in gas
- It cannot be used with oxidizing and reducing environment

### Secondary reference electrodes:

- Due to the limitations of standard hydrogen electrode some other electrodes whose electrode potentials are accurately known and remain stable over a long period of time and can be easily assembled. With respect to these electrodes , electrode potentials of other electrodes can be assigned

e.g., **Calomel electrode, silver silver chloride electrode**

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

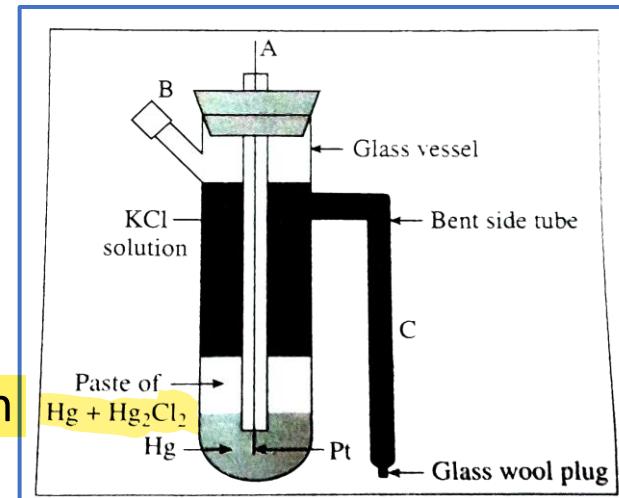
### Secondary Reference electrodes:

#### Calomel electrode

- Most widely used reference electrode
- Metal-insoluble salt –ion electrode

#### Construction:

- A glass tube containing a layer of mercury over which a paste of insoluble salt  $\text{Hg}_2\text{Cl}_2$  (calomel) + Hg and the next layer is a solution of KCl
- A Pt wire dipped in Hg provides electrical contact
- Tube is fitted with a side tube to fill KCl solution of known concentration and another side tube which connects to the salt bridge



<https://doubtnut.com/question-answer-chemistry/describe-the-construction-and-working-of-the-calomel-electrode-96607395>

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria



- $\text{Hg}/\text{Hg}_2\text{Cl}_2(\text{s})/\text{Cl}^-$

**Working :**

- Can act as anode or cathode depending on the nature of the electrode with which it is coupled

As anode:



As cathode:



# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria



Applying Nernst's equation



$$E = E^\circ - 2.303RT/2F \log [\text{Cl}^-]^2$$

at 298K

$$E = E^\circ - 0.0591 \log [\text{Cl}^-]$$

- Electrode is reversible to chloride ions
- Electrode potential depends on chloride ion concentration

Types of calomel electrodes:

[KCl]	Name	Electrode potential at 298K
0.1M	Decinormal electrode	0.3358 V
1M	Normal electrode	0.2824 V
Saturated solution of KCl	Saturated Calomel Electrode(SCE)	0.2422 V



**THANK YOU**

---

**Lata Pasupulety**

Department of Science and Humanities

**[latapasupulety@pes.edu](mailto:latapasupulety@pes.edu)**

+91 80 6666 3333 Extn 759



**PES**  
UNIVERSITY

CELEBRATING 60 YEARS

# ENGINEERING CHEMISTRY

---

**Lata Pasupulety**

Department of Science and Humanities

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

---



### *Class content:*

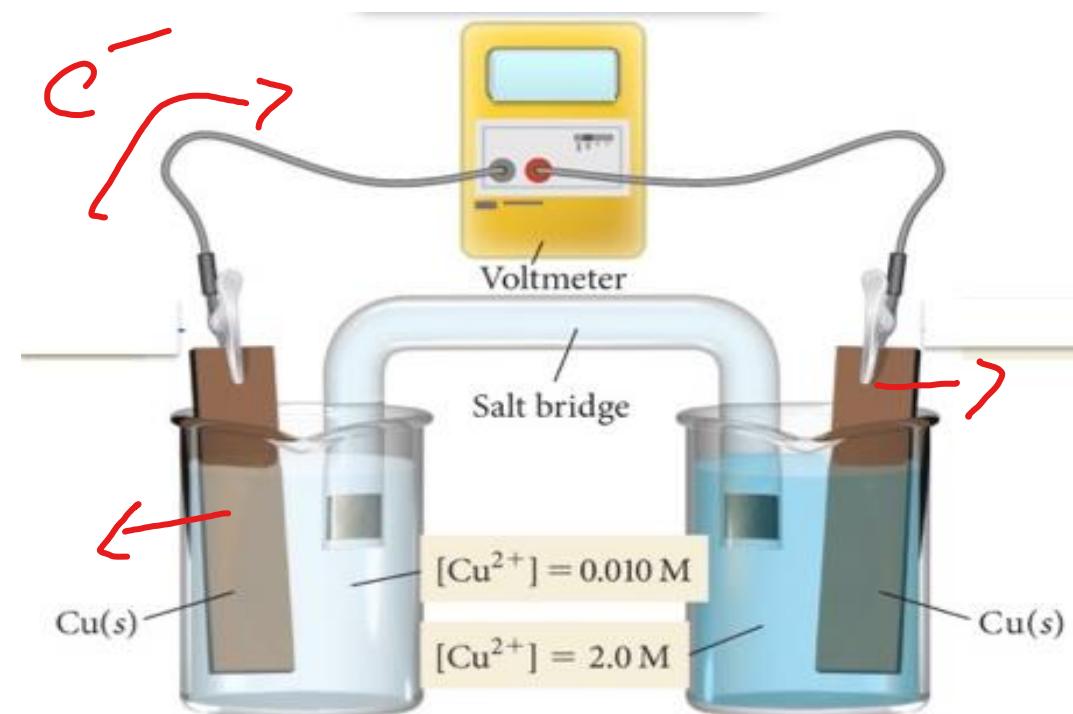
- ***Concentration cells***
  - *Types of concentration cells*
    - *Electrolyte concentration cells*
    - *Electrode concentration cells*
- ***Ion-selective electrodes***
  - *Types of ion – selective electrodes*
  - *Electrode potential for an ion-selective electrode*

# ENGINEERING CHEMISTRY

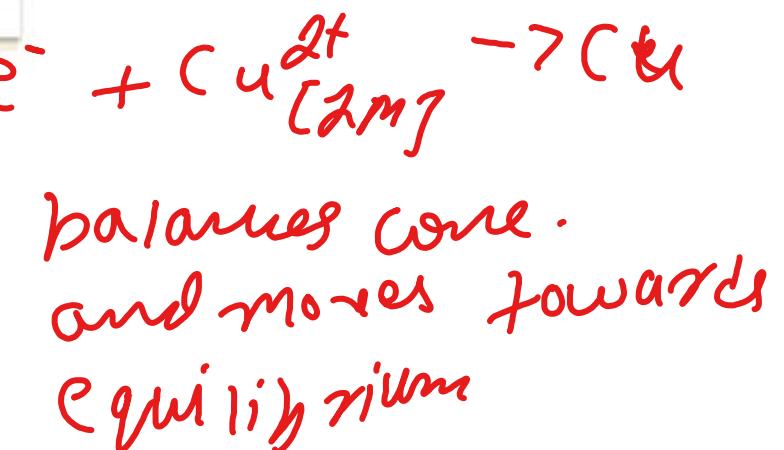
## Module 1- Electrochemical equilibria

### Concentration cells:

- An electrochemical cell in which identical electrodes are in contact with a solution of identical species but of different concentration



loses  $e^-$   
to increase  
(one-



# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

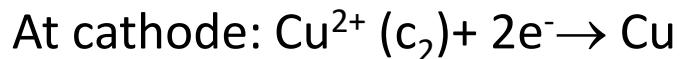
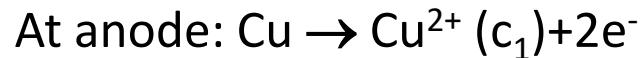
- In this cell 2 copper electrodes are immersed in copper sulphate solutions of concentration  $c_1$  &  $c_2$ , such that  $c_2 > c_1$
- An electrolyte has spontaneous tendency to diffuse from a solution of higher concentration to a solution of lower concentration which is the **driving force** for development of potential
- Oxidation takes place at anode and reduction takes place at cathode
- e.g.,  $\text{Cu}/\text{Cu}^{2+}(c_1) // \text{Cu}^{2+}(c_2)/\text{Cu}$

Oxidn  
→ lower conc.

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

### Reactions :



### Expression for cell potential:

The emf of the cell =  $E_{\text{cathode}} - E_{\text{anode}}$

$$E_{\text{cathode}} = E^{\circ} + \frac{2.303RT}{nF} \log c_2$$

$$E_{\text{anode}} = E^{\circ} + \frac{2.303RT}{nF} \log c_1$$

$$E_{\text{cell}} = \left( E^{\circ} + \frac{2.303RT}{nF} \log c_2 \right) - \left( E^{\circ} + \frac{2.303RT}{nF} \log c_1 \right)$$

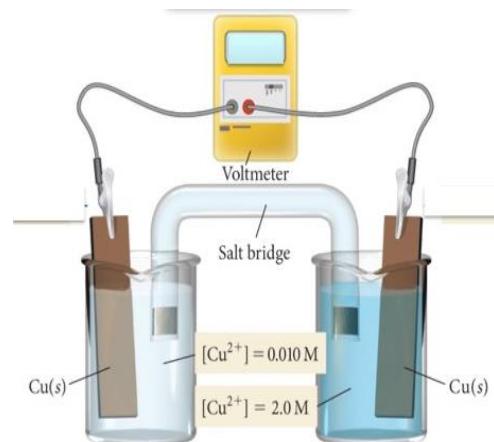
$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \left( \frac{c_2}{c_1} \right)$$

$$\text{At 298K, } E_{\text{cell}} = \frac{0.0591}{n} \log \left( \frac{c_2}{c_1} \right)$$

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

- The emf of the cell is positive only if  $c_2 > c_1$   
i.e., conc of metal ion at cathode > conc. of metal ion at anode
- The emf of the cell depends upon the ratio  $c_2/c_1$
- When  $c_2 = c_1$ , the emf of the cell becomes zero
- During working of the cell, concentration of ions increases at anode decreases at cathode
- When current is drawn from the cell  $c_1$  increases and  $c_2$  decreases
- The cell can operate only as long as the concentration terms are different



# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

### Types of concentration cells:

- Electrolyte concentration cell
- Electrode concentration cell

### Electrolyte concentration cell:

- Electrolyte concentration cell consists of two same electrodes that are dipped in the same electrolyte but with different concentrations of electrolytes
- $\text{Cu}/\text{Cu}^{2+}(c_1)/\text//\text{Cu}^{2+}(c_2)/\text{Cu}$
- Cell potential is given by

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log\left(\frac{c_2}{c_1}\right)$$

### Electrode concentration cell

- Electrode concentration cell consists of two identical electrodes of different activity which are dipped in the same solution of electrolyte
- $\text{Na-Hg}(c_1)/\text{Na}^+/\text{Na-Hg}(c_2)$
- Cell potential is given by

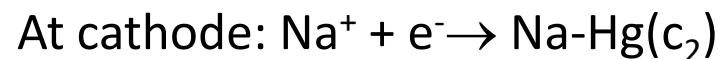
$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{\text{Na-Hg}(c_1)}{\text{Na-Hg}(c_2)}$$

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

- $\text{Na}-\text{Hg}(c_1)/\text{Na}^+/\text{Na}-\text{Hg}(c_2)$  :

Reactions are :



$$\text{Cell potential} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cathode}} = E^{\circ} - \frac{2.303RT}{nF} \log \frac{\text{Na}-\text{Hg}(c_2)}{\text{Na}^+}$$

$$E_{\text{anode}} = E^{\circ} - \frac{2.303RT}{nF} \log \frac{\text{Na}-\text{Hg}(c_1)}{\text{Na}^+}$$

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{\text{Na}-\text{Hg}(c_1)}{\text{Na}-\text{Hg}(c_2)}$$

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria



- $\text{Pt}/\text{H}_2(\text{p}_1 \text{ atm})/\text{H}^+/\text{H}_2(\text{p}_2 \text{ atm})/\text{Pt}$  :

Nernst Equation:

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{p_1}{p_2}$$

- $\text{Pt}/\text{Cl}_2(\text{p}_1 \text{ atm})/\text{Cl}^-/\text{Cl}_2(\text{p}_2 \text{ atm})/\text{Pt}$  :

Nernst Equation:

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{p_2}{p_1}$$

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

---



### Ion selective electrodes (ISE)

- Selectively respond to a **specific ion** in a mixture
- Potential developed is a **function of concentration** of that ion
- Have a **membrane** which is capable of exchanging the specific ion **with solution** with which it is in contact
- **Membrane electrodes**  
e.g., **glass electrode**

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

---

### Types of Ion selective electrodes :

Electrodes are classified based on the membrane material

- **Crystalline / solid state membrane electrodes:**

Single crystal  $\text{LaF}_3$  selective to  $\text{F}^-$

Polycrystalline such as  $\text{Ag}_2\text{S}$  selective to  $\text{S}^{2-}$

- **Non-crystalline membrane electrodes:**

e.g., Glass membrane selective to  $\text{H}^+$ ,  $\text{Na}^+$

- **Liquid membrane electrodes:**

An ion-exchanger is dissolved in a viscous organic liquid membrane; used for  $\text{Ca}^+$ ,  $\text{K}^+$

- **Immobilised liquid in a rigid polymer:**

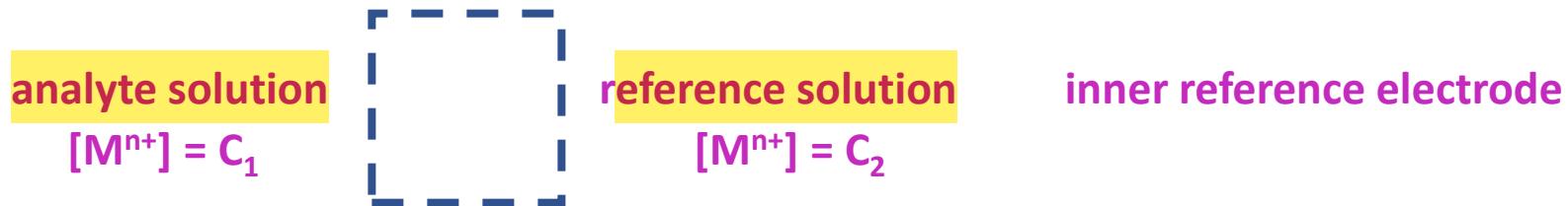
e.g., immobilized ion exchanger in PVC matrix ; used for  $\text{Ca}^+$ ,  $\text{NO}_3^-$

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

### Electrode potential of an ion-selective electrode

Schematic representation:



boundary potential is

$$E_j = \frac{2.303RT}{nF} \log\left(\frac{C_1}{C_2}\right)$$

since concentration of reference solution  $C_2$  is constant

$$E_j = \frac{2.303RT}{nF} \log C_1 + K$$

where

$$K = -\frac{2.303RT}{nF} \log C_2$$

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

Overall potential of the membrane electrode is given by

$$E_M = E_j + E_{ref}$$

since  $E_j = \frac{2.303RT}{nF} \log C_1 + K$

$$E_M = \frac{2.303RT}{nF} \log C_1 + K + E_{ref}$$

$$E_M = E^o_M + \frac{2.303RT}{nF} \log C_1 \quad \text{where} \quad E^o_M = K + E_{ref}$$

At 298K,  $E_M = E^o_M + \frac{0.0591}{n} \log C_1$

Membrane electrode is coupled with an external reference electrode

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria



External ref. electrode/Analyte/membrane/ ref. solution/Internal ref. electrode

$$\text{Cell potential} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = E_{\text{membrane}} - E_{\text{ext.ref.electrode}}$$

$E_{\text{cell}}$  can be measured,  $E_{\text{ext.ref.electrode}}$  is known

$E_{\text{membrane}}$  can be determined

Since  $E_M = E^{\circ}_M + \frac{0.0591}{n} \log C_1$ ,  $C_1$  can be determined

The disadvantage of an ion-selective electrode is that the **membrane offers very high resistance** so ordinary potentiometers cannot be used; special type of potentiometers have to be used.

### Applications :

Used to determine concentration of number of cations and anions such as  $H^+$ ,  $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Pb^{2+}$ ,  $Cu^{2+}$ ,  $Mg^{2+}$ ,  $CN^-$ ,  $NO_3^-$ ,  $F^-$  etc



# THANK YOU

---

**Lata Pasupulety**

Department of Science and Humanities

**[latapasupulety@pes.edu](mailto:latapasupulety@pes.edu)**

+91 80 6666 3333 Extn 759



**PES**  
UNIVERSITY

CELEBRATING 60 YEARS

# ENGINEERING CHEMISTRY

---

**Lata Pasupulety**

Department of Science and Humanities

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

---



### *Class content:*

- *Glass electrode*
  - *Construction*
  - *Working*
  - *Determination of pH*

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

---



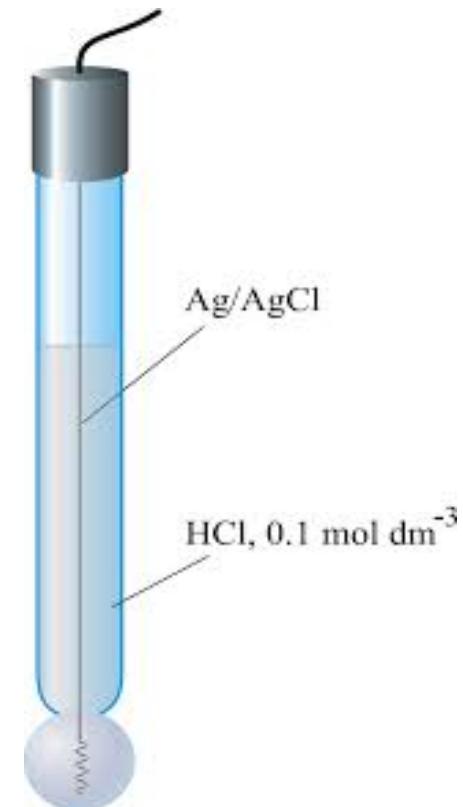
### Glass electrode

- Ion-selective electrode
- Responds to Hydrogen ion
- pH sensitive; can be used to determine pH of a solution
- Consists of a glass membrane which is capable of exchanging  $\text{H}^+$  ions

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

- Construction:
- Glass tube , the end of which is a bulb of **very thin glass membrane**
- Glass bulb is made up of special type of glass, **CORNING 015**
- The glass bulb is filled with **solution of known pH** which is the reference solution
- A **silver - silver chloride electrode** is dipped inside the reference solution serves as **internal reference electrode** and also provides external electrical contact
- The electrode is immersed in a **solution containing  $H^+$**  which is the analyte
- **Ag/AgCl/HCl/glass**



Source:<https://glossary.periodni.com/glossary.php?en=glass+electrode>

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

Working:

analyte solution



reference solution

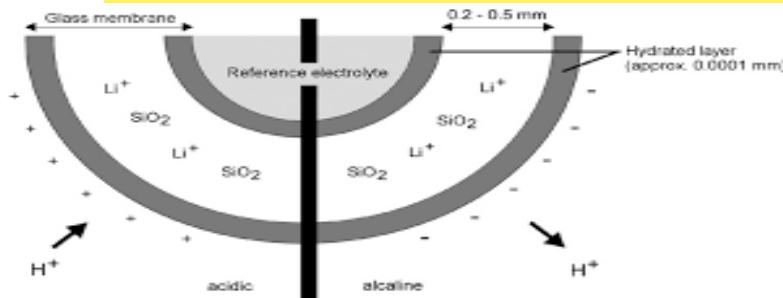
Ag-AgCl electrode

$$[H^+] = C_1$$

$$[H^+] = 0.1\text{M HCl} = C_2$$



- The inner and outer surfaces of the glass membrane can exchange  $H^+$  ions with the solution they are in contact with



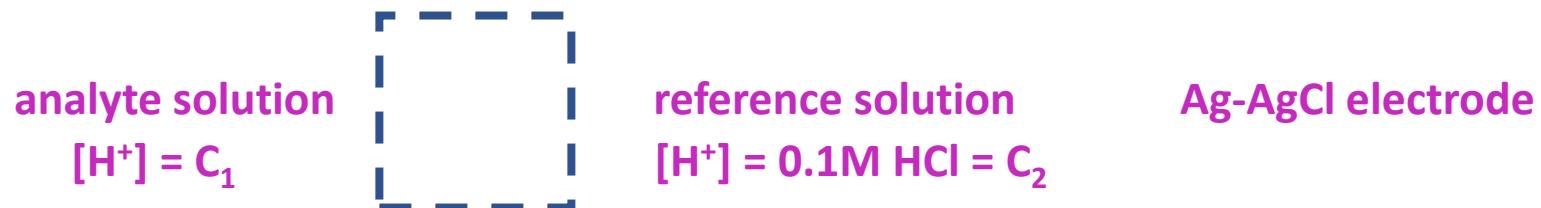
Source:[http://www.metrohmsiam.com/teachingresearch/TRL 25/TRL25\\_955207\\_80155013.pdf](http://www.metrohmsiam.com/teachingresearch/TRL 25/TRL25_955207_80155013.pdf)

- The hydrated glass membrane brings about ion exchange reaction between singly charged cations in the interstices of glass lattice and protons from the solution
- A potential is developed, which is a function of  $H^+$  of the solution

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

Electrode potential of a glass electrode :



boundary potential is       $E_b = \frac{2.303RT}{nF} \log\left(\frac{C_1}{C_2}\right)$

since concentration of reference solution,  $C_2$  is constant

$$E_b = L' + \frac{2.303RT}{nF} \log C_1 \qquad \text{where} \qquad L' = -\frac{2.303RT}{nF} \log C_2$$

At 298K,     $E_b = L' + \frac{0.0591}{n} \log[H^+]$       since for  $H^+$ ,  $n = 1$

$$E_b = L' - 0.0591pH$$

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

The glass electrode potential has 3 components

1. The boundary potential
2. The potential of internal reference electrode
3. Asymmetric potential

$$E_G = E_b + E_{\text{ref}} + E_{\text{asymmetric}}$$

- Asymmetric potential arises due to difference in responses of inner and outer surfaces of the glass bulb, due to differing conditions of stress on two glass surfaces

$$\begin{aligned} E_G &= E_b + E_{\text{ref}} + E_{\text{asymmetric}} ; \quad E_b = L' + \frac{0.0591}{n} \log[H^+] \\ &= L' + \frac{0.0591}{n} \log[H^+] + E_{\text{ref}} + E_{\text{asymmetric}} \\ &= E_G^0 + 0.0591 \log [H^+] \quad \text{where } E_G^0 = L' + E_{\text{ref}} + E_{\text{asymmetric}} \end{aligned}$$
$$E_G = E_G^0 - 0.0591 \text{pH}$$

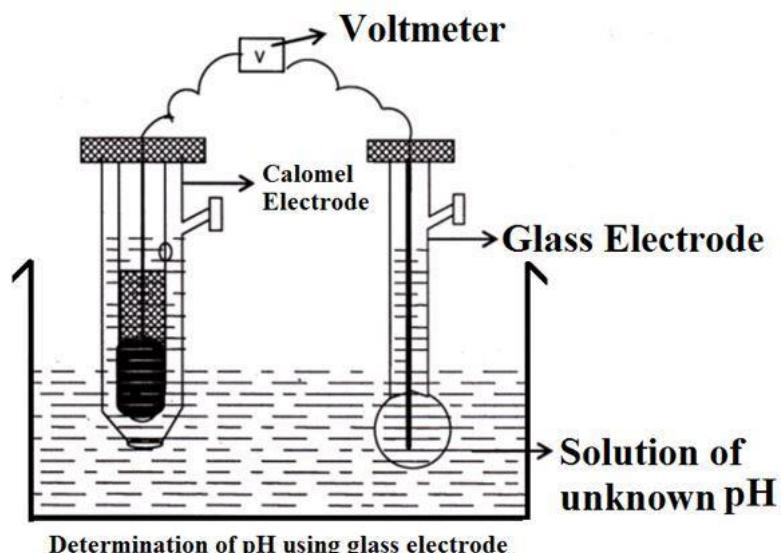
# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

Determination of pH using glass electrode:

- Glass electrode is combined with an external reference electrode

**Hg/Hg<sub>2</sub>Cl<sub>2</sub>/Cl<sup>-</sup>//analyte solution/glass/0.1N HCl/AgCl/Ag**



Source:<https://utkarshiniedu.wordpress.com/2016/12/22/lecture-1-108-ion-selective-electrodes/>

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

### Determination of pH using glass electrode:

- The emf of the cell is determined potentiometrically

$$E_{\text{cell}} = E_G - E_{\text{calomel}} ; \quad E_G = E^0_G - 0.0591 \text{pH}$$

$$= E^0_G - 0.0591 \text{pH} - E_{\text{calomel}}$$

$$\text{pH} = \frac{E^0_G - E_{\text{calomel}} - E_{\text{cell}}}{0.0591}$$

- To evaluate  $E^0_G$  the glass electrode is dipped in a **solution of known pH(buffer solution)** and combined with calomel electrode, the emf of the cell is measured from which  $E^0_G$  can be evaluated

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

---

### Applications of glass electrode:

Used extensively in chemical, industrial, agricultural and biological labs

### Advantages of glass electrode :

- Can be used in oxidizing and reducing environments and metal ions
- Does not get poisoned
- Can be used for very small volumes
- Accurate results can be obtained between pH 1 to 9 by ordinary electrodes. However by using special glass electrodes pH 1 to 14 can be measured with accuracy
- Simple to operate and can be used with portable instruments

# ENGINEERING CHEMISTRY

## Module 1- Electrochemical equilibria

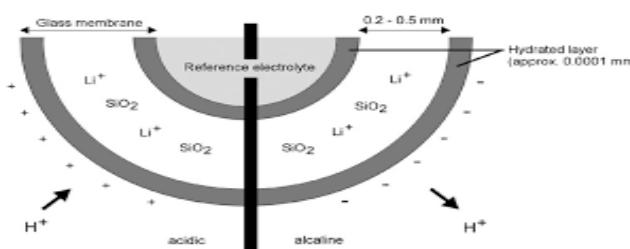
### Disadvantages of glass electrode:

- Because of high resistance of glass, a simple potentiometer cannot be used. It requires sensitive potentiometer for emf measurements
- Glass membrane is very delicate, hence has to be handled carefully
- At very high pH levels usually over a pH of 9 , **Alkaline error** is observed



When the Sodium ion level is relatively high, some of the  $\text{H}^+$  ions in the gel layer around the sensitive electrode membrane are replaced by  $\text{Na}^+$  ions

The electrode may eventually respond to  $\text{Na}^+$  instead of  $\text{H}^+$  ions, giving a false lower pH value than the actual value





# THANK YOU

---

**Lata Pasupulety**

Department of Science and Humanities

**[latapasupulety@pes.edu](mailto:latapasupulety@pes.edu)**

+91 80 6666 3333 Extn 759



**PES**  
UNIVERSITY

CELEBRATING 60 YEARS

# ENGINEERING CHEMISTRY

---

**Lata Pasupulety**

Department of Science and Humanities

# ENGINEERING CHEMISTRY

## Module 1 – Electrochemical Equilibria

---



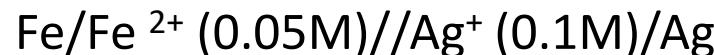
### *Class content:*

- *Numericals on electrochemistry*
  - *Nernst equation*
  - *Ion selective electrode*

# ENGINEERING CHEMISTRY

## Module 1 – Electrochemical Equilibria

1. For the given cell:



- (i) Write the overall cell reaction  
(ii) Calculate  $E_{\text{cell}}^{\circ}$  and  $E_{\text{cell}}$  at  $25^{\circ}\text{C}$  *→ Room Temp.*  
(Given :  $E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.44\text{V}$ ;  $E_{\text{Ag}^+/\text{Ag}}^{\circ} = 0.80\text{V}$ )

Sol. Anode :  $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$

Cathode :  $2\text{Ag}^+ + 2\text{e}^- \rightarrow 2\text{Ag}$

Overall reaction :  $\text{Fe} + 2\text{Ag}^+ \rightarrow \text{Fe}^{2+} + 2\text{Ag}$

$$E_{\text{cell}}^{\circ} = E_{\text{C}}^{\circ} - E_{\text{A}}^{\circ} = 0.80 + 0.44 = 1.24\text{V}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Fe}^{2+}][\text{Ag}]^2}{[\text{Fe}][\text{Ag}^+]^2}$$

$$E_{\text{cell}} = 1.24 - \frac{0.0591}{2} \log \left( \frac{[0.05]}{[0.1]^2} \right)$$

$$E_{\text{cell}} = 1.2193\text{V}$$

# ENGINEERING CHEMISTRY

## Module 1 – Electrochemical Equilibria

---



2. For the following concentration cell:



Calculate potential of the cell at 25°C.

Sol.

$$E_{cell} = \frac{0.0591}{n} \log \frac{p_{H_2(anode)}}{p_{H_2(cathode)}}$$

$$E_{cell} = \frac{0.0591}{n} \log \frac{8}{2}$$

$$E_{cell} = 0.01779\text{V}$$

# ENGINEERING CHEMISTRY

## Module 1 – Electrochemical Equilibria



3. A decinormal calomel electrode as cathode is coupled with a saturated calomel electrode as anode to form a cell. Write the cell representation and calculate the concentration of  $\text{Cl}^-$  ion in the saturated calomel electrode, if the cell potential measured is 0.0988 V at 25°C.

Sol.



$$E_{\text{cell}} = E_R - E_L$$

$$= [E^0 - 0.0591 \log (0.1)] - [E^0 - 0.0591 \log(x)]$$

$$\frac{0.0988}{0.0591} = \log \frac{x}{0.1}$$

$$1.6717 - 1 = \log(x)$$

$$x = \text{Antilog}(0.6717)$$

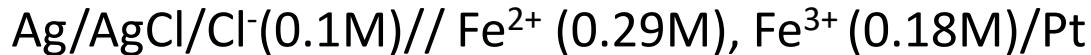
$$x = 4.69\text{M}$$

# ENGINEERING CHEMISTRY

## Module 1 – Electrochemical Equilibria



4. For the following cell:

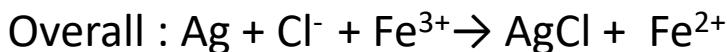
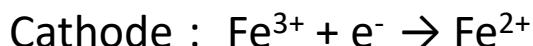


(i) Write the half cell reactions and overall cell reaction.

(ii) Calculate  $E_{\text{Cell}}^{\circ}$  and  $E_{\text{Cell}}$  at 298 K

(Given:  $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} = 0.77 \text{ V}$ ,  $E_{\text{Calomel}}^{\circ} = 0.222 \text{ V}$ ,  $R = 8.314 \text{ J/K/mol}$ ,  $F = 96500 \text{ C/mol}$ )

**Sol.** (i) Anode:  $\text{Ag} + \text{Cl}^- \rightarrow \text{AgCl} + \text{e}^-$



$$(ii) E_{\text{cell}}^{\circ} = E_{\text{C}}^{\circ} - E_{\text{A}}^{\circ} = 0.77 - 0.222 = \mathbf{0.548 \text{ V}}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \left[ \frac{[\text{Fe}^{2+}]}{([\text{Fe}^{3+}][\text{Cl}^-])} \right]$$

$$E_{\text{cell}} = 0.548 - \frac{0.0591}{1} \log \left[ \frac{[0.29]}{[0.18]x[0.1]} \right]$$

$$E_{\text{Cell}} = \mathbf{0.4767 \text{ V}}$$

# ENGINEERING CHEMISTRY

## Module 1 – Electrochemical Equilibria

---

5. Calculate the EMF of the following cell at 25°C.



(Given : R = 8.314 J/K/mol, F = 96500 C/mol)

Sol.

$$E_{cell} = \frac{0.0591}{n} \log \frac{[\text{M}^{n+}(\text{cathode})]}{[\text{M}^{n+}(\text{anode})]}$$

$$E_{cell} = \frac{0.0591}{n} \log \left[ \frac{(0.12)}{0.05} \right]$$

$$n = 3 ,$$

$$E_{cell} = 0.00749\text{V}$$

# ENGINEERING CHEMISTRY

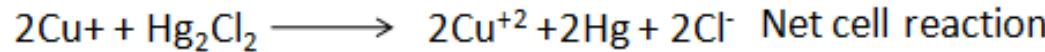
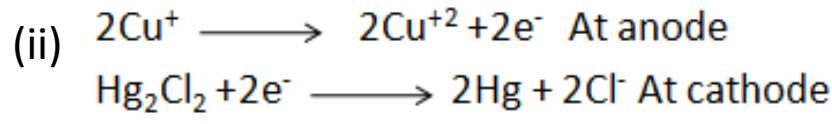
## Module 1 – Electrochemical Equilibria

6. A decinormal calomel electrode is used to determine the potential of the following redox electrode : Pt/Cu<sup>2+</sup>(0.58 M),Cu<sup>+</sup>(0.08M)

- (i) Write cell representation.
- (ii) Write the reactions at the electrodes
- (iii) Calculate E<sup>0</sup><sub>cell</sub> and E<sub>cell</sub> at 298 K.

(Given : E<sup>0</sup><sub>Hg/Hg<sub>2</sub>Cl<sub>2</sub>/Cl<sup>-</sup></sub> = 0.281V , E<sub>Cu<sup>2+</sup>/Cu<sup>+</sup></sub> = 0.153 V)

**Sol.** (i) Pt/Cu<sup>2+</sup>(0.58 M),Cu<sup>+</sup>(0.08M)//Cl<sup>-</sup>(0.1 M)/Hg<sub>2</sub>Cl<sub>2</sub>/Hg



(iii)  $E_{cell}^0 = E_C^0 - E_A^0 = 0.281 - 0.153 = 0.128 \text{ V}$

$$E_{cell} = E_{cell}^0 - \frac{0.0591}{n} \log \left[ \frac{([Cl^-]^2 [Cu^{2+}]^2)}{([Cu^+]^2)} \right]$$

$$E_{cell} = 0.1362 \text{ V}$$

$$E = E_{cell}^0 - \frac{0.0591}{2} \log \frac{0.58^2 \times 0.1^2}{0.08^2}$$

# ENGINEERING CHEMISTRY

## Module 1 – Electrochemical Equilibria



7. For the following cell:



- Write the half cell reactions.
- Calculate  $E_{\text{cell}}^{\circ}$  and  $E_{\text{cell}}$  at 298K .

(Given  $E_{\text{Au}^{+3}/\text{Au}}^{\circ} = 1.52\text{V}$ ,  $E_{\text{Fe}^{+2}/\text{Fe}}^{\circ} = -0.44\text{V}$ ,  $R = 8.314 \text{ J/K/mol}$ ,  $F = 96500\text{C/mol}$ )

Sol. i) Half cell reactions



(ii)  $E_{\text{cell}}^{\circ} = E_{\text{C}}^{\circ} - E_{\text{A}}^{\circ} = 1.52 + 0.44 = 1.96 \text{ V}$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \left[ \frac{[\text{Fe}^{+2}]^3}{[\text{Au}^{+3}]^2} \right]$$

$$E_{\text{cell}} = 1.96 - \frac{0.0591}{6} \log \left[ \frac{[0.1]^3}{[0.5]^2} \right]$$

$$E_{\text{cell}} = 1.9836 \text{ V}$$

# ENGINEERING CHEMISTRY

## Module 1 – Electrochemical Equilibria



8. A glass electrode is coupled with saturated calomel electrode to measure unknown pH. The cell potentials measured are 0.215V and 0.385V in contact with a solution of pH = 7 and with solution of unknown pH respectively. Calculate the pH of unknown solution.

Given  $E_{SCE} = 0.244\text{V}$

Sol. 
$$\begin{aligned} E_G^o &= E_{cell} + 0.0591\text{pH} + E_{SCE} \\ &= 0.215 + 0.0591 \times 7 + 0.244 \\ &= 0.8727 \text{ V} \end{aligned}$$

$$pH = \frac{E_G^o - E_{SCE} - E_{cell}}{0.0591}$$

$$pH = \frac{0.8727 - 0.244 - 0.385}{0.0591}$$

$$\text{pH} = 4.12$$



**PES**  
UNIVERSITY

CELEBRATING 60 YEARS

## THANK YOU

---

**Lata Pasupulety**

Department of Science and Humanities

**latapasupulety@pes.edu**

+91 80 6666 3333 Extn 759



**PES**  
UNIVERSITY

CELEBRATING 60 YEARS

# ENGINEERING CHEMISTRY

---

**Lata Pasupulety**

Department of Science and Humanities

# ENGINEERING CHEMISTRY

## Module 2- Corrosion Chemistry

---



### ***Module content:***

- *Electrochemical Theory of corrosion*
- *Types of corrosion*
- *Factors affecting rates of corrosion*
- *Corrosion control*

# ENGINEERING CHEMISTRY

## Module 2- Corrosion Chemistry

---



### *Class content:*

- *Corrosion*
- *Types of corrosion*
- *Electrochemical Theory of corrosion*
- *Corrosion of Iron*

# ENGINEERING CHEMISTRY

## Module 2- Corrosion Chemistry

---

### Corrosion

- The destruction or deterioration & consequent loss of metal through **direct chemical or electrochemical attack** by the environment
- Most metals except very noble ones, corrode on contact with water (and moisture in the air), acids, bases, salts, oils, aggressive metal polishes, and other solid and liquid chemicals
- **Spontaneous process**
- Causes **indirect losses**

# ENGINEERING CHEMISTRY

## Module 2- Corrosion Chemistry

Pure metal → undesirable products

- **Rusting of iron** - a reddish brown scale formation on iron and steel objects
- Due to formation of **hydrated ferric oxide** ( $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ )
- **Scaling of Copper** - Green scales formed on copper articles
- Due to formation of **basic cupric carbonate** ( $\text{CuCO}_3 + \text{Cu}(\text{OH})_2$ )



The Statue of Liberty is covered with a copper skin, and was originally brown, as shown in this painting



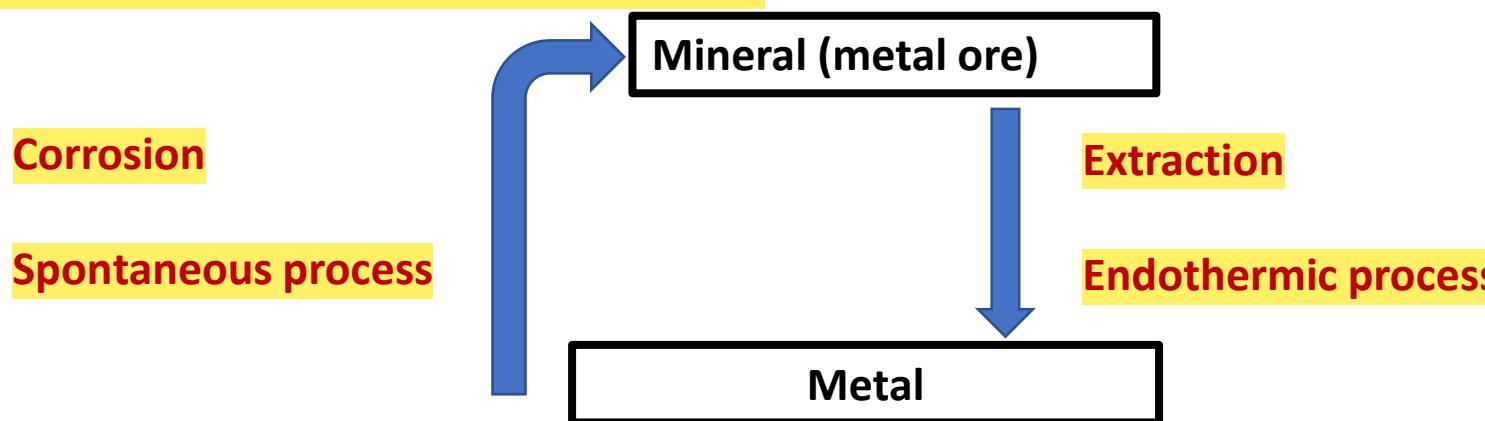
Exposure to the elements has resulted in the formation of the blue-green **patina** seen today

# ENGINEERING CHEMISTRY

## Module 2- Corrosion Chemistry

### Why do metals undergo corrosion?

- Most metals occur in nature in the **form of their compounds** such as oxides, sulfides, carbonates, chlorides
- Metals are extracted from these ores by **reduction** which is an **endothermic process**, energy being supplied in the form of heat or electrical energy
- Pure metals are relatively at **higher energy state** compared to their corresponding ores, and they have a natural tendency to revert back to their combined state



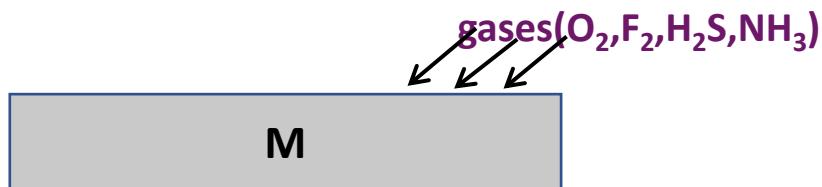
# ENGINEERING CHEMISTRY

## Module 2- Corrosion Chemistry

### Types of corrosion

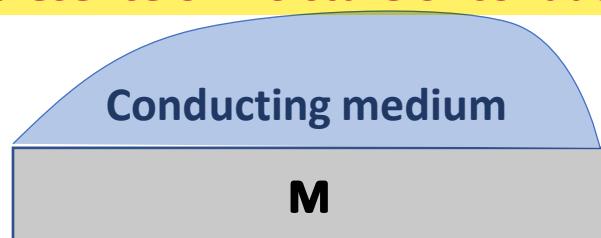
- **Dry corrosion :**

- Direct chemical attack due to affinity of the metal to certain gases
- In the absence of the electrolytic medium



- **Wet corrosion :**

- Electrochemical attack on the metal
- in the presence of moisture or conducting medium



# ENGINEERING CHEMISTRY

## Module 2- Corrosion Chemistry

### Electrochemical theory of corrosion

- A large number of **tiny galvanic cells** are formed due to the formation of separate anodic and cathodic regions on the metal surface
- **At the anodic region**, metal undergoes oxidation and gets converted into its ions, liberating electrons and the **metal undergoes corrosion**
- **At the cathodic region**, reduction takes place but since the metal cannot be reduced further, metal atoms are **unaffected by corrosion**

Anode

Cathode

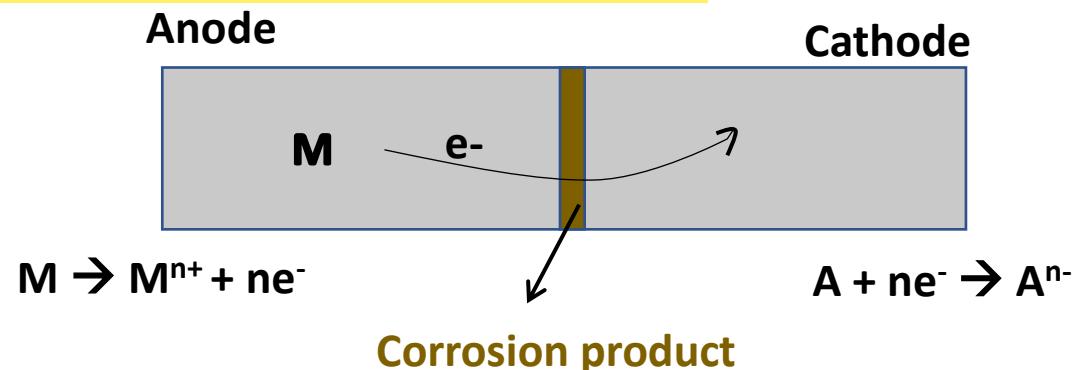
M



# ENGINEERING CHEMISTRY

## Module 2- Corrosion Chemistry

- The electrons liberated at the anodic region **migrate** to the cathodic region constituting a **small corrosion current**
- The **metal ions** formed at the anode and **some anions** formed at the cathode diffuse towards each other through the conducting medium and form a **corrosion product** somewhere between anode and the cathode
- Corrosion of metal continues as long as both **anodic and cathodic reactions take place simultaneously**



# ENGINEERING CHEMISTRY

## Module 2- Corrosion Chemistry

---

### Reactions:

- Anode:



e.g., when iron undergoes corrosion,



- Cathode:

- Liberation of hydrogen
- Absorption of oxygen

# ENGINEERING CHEMISTRY

## Module 2- Corrosion Chemistry

---

- Liberation of hydrogen

- In acidic medium



- In neutral or alkaline medium



- Absorption of oxygen

- In acidic medium



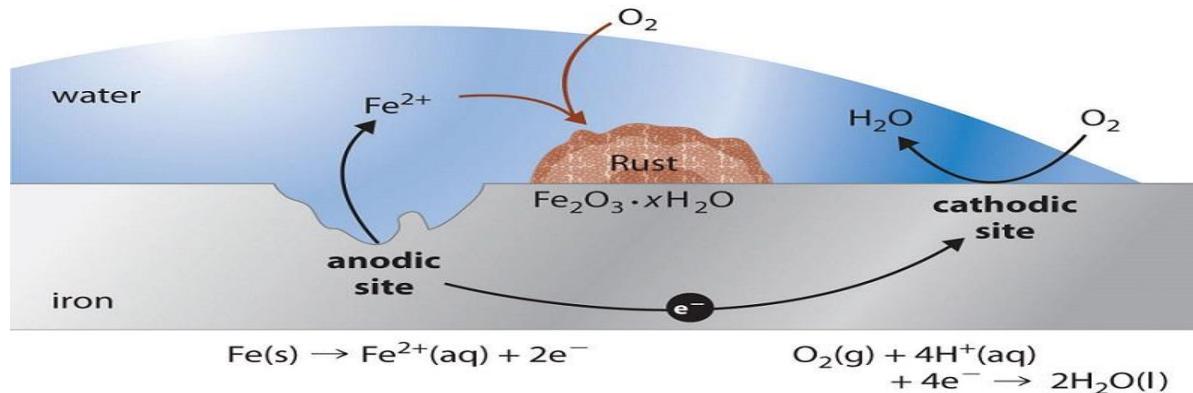
- In neutral or alkaline medium



# ENGINEERING CHEMISTRY

## Module 2- Corrosion Chemistry

### Corrosion of Iron:



Source: [https://chem.libretexts.org/Bookshelves/General\\_Chemistry/Book%3A\\_Chem1\\_\(Lower\)/16%3A\\_Electrochemistry/16.08%3A\\_Electrochemical\\_Corrosion](https://chem.libretexts.org/Bookshelves/General_Chemistry/Book%3A_Chem1_(Lower)/16%3A_Electrochemistry/16.08%3A_Electrochemical_Corrosion)



$\text{Fe}^{2+}$  and  $\text{OH}^-$  ions move towards one another and  $\text{Fe(OH)}_2$  is formed somewhere between anode and cathode regions



# ENGINEERING CHEMISTRY

## Module 2- Corrosion Chemistry

- In an **oxidizing environment**,  $\text{Fe(OH)}_2$  is oxidized to hydrated ferric oxide and is known as **yellow rust**



- In the **presence of limited oxygen**,  $4\text{Fe(OH)}_2$  is converted into **magnetic oxide of iron ( $\text{Fe}_3\text{O}_4$ )** and is known as **black rust**





**THANK YOU**

---

**Lata Pasupulety**

Department of Science and Humanities

**latapasupulety@pes.edu**

+91 80 6666 3333 Extn 759



## ENGINEERING CHEMISTRY

---

**Asha A**

Department of Science and Humanities

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---



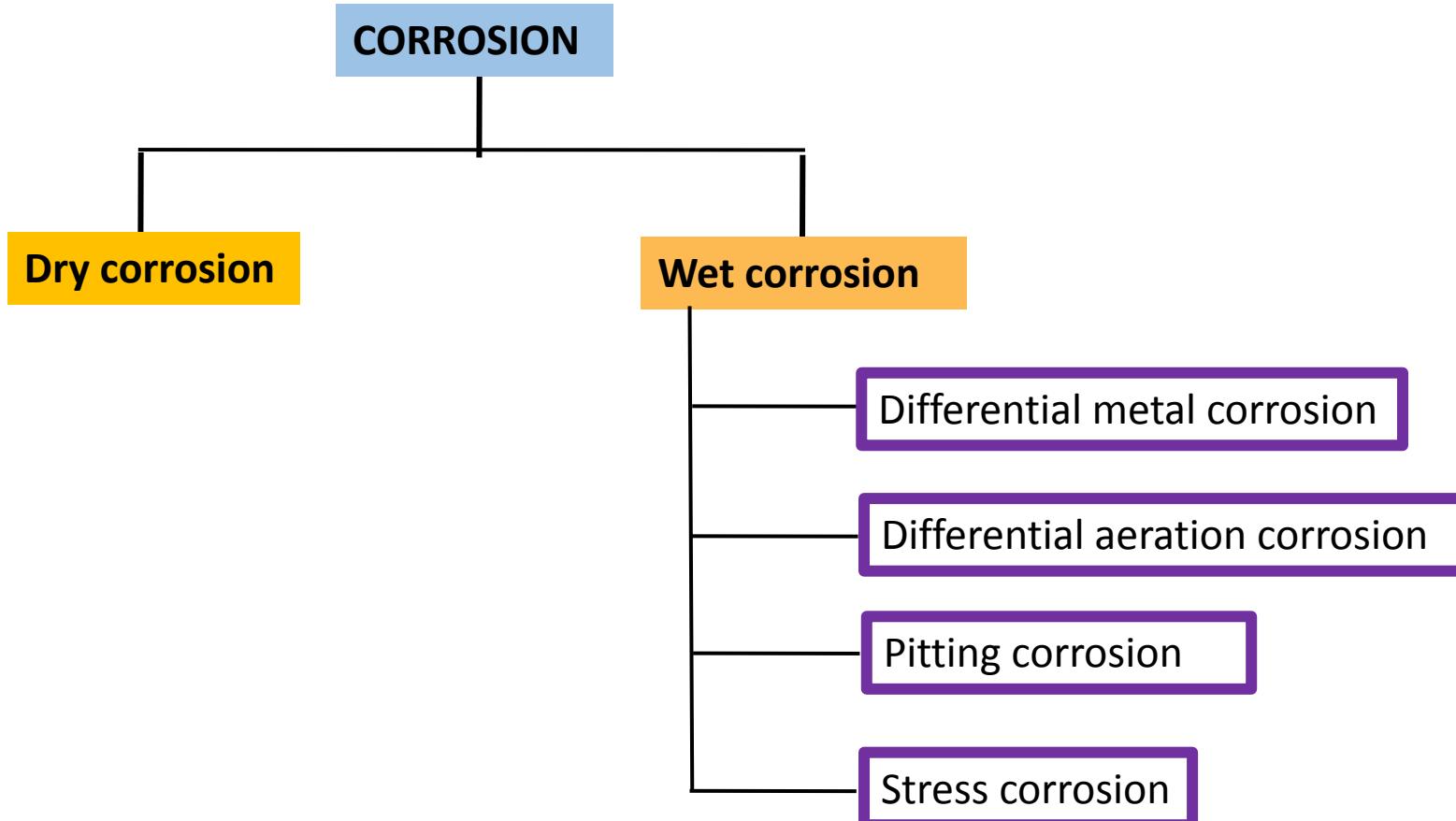
### *Class content:*

- *Types of electrochemical corrosion*
  - *Differential metal corrosion*
  - *Differential aeration corrosion*

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

### Types of corrosion



### Differential metal corrosion :

- Also called **galvanic corrosion**
- When **two dissimilar metals** are in contact with each other and are exposed to a corrosive environment
- The two metals differ in their **electrode potentials**. The metal with lower electrode potential acts as **anode** and the other metal with higher electrode potential acts as **cathode**
- The anodic metal undergoes **oxidation** and gets corroded. The cathodic metal remains unaffected
- The driving force for corrosion is the **difference in electrode potentials** of the two metals

# ENGINEERING CHEMISTRY

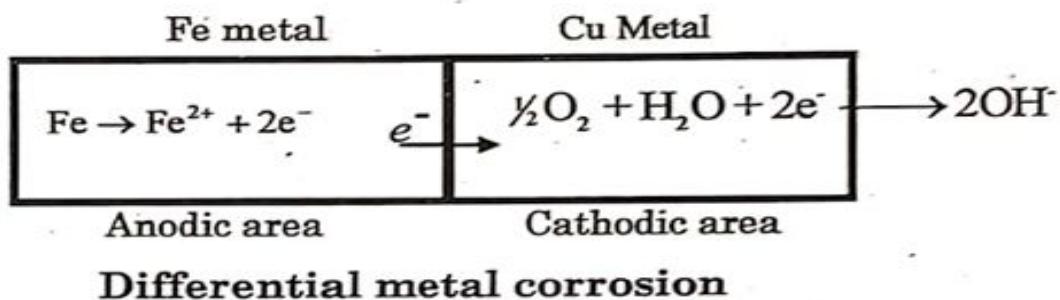
## Module 6- Corrosion Chemistry

### Reactions:



### Examples:

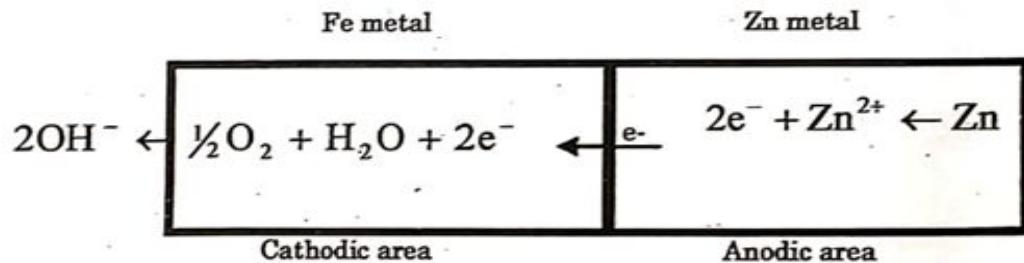
- Iron in contact with copper
- Standard electrode potential of Fe (-0.44 V)  
Cu (0.34 V)



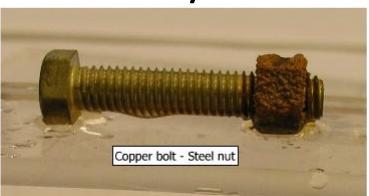
# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

- Iron in contact with zinc
- Standard electrode potential of Zn (-0.76 V)  
Fe (-0.44 V)



- Steel screws/rivets in copper sheet



Source:<https://faculty.kfupm.edu.sa/me/hussaini/corrosion%20engineering/model-03.htm>

- Steel pipe connected to copper plumbing



Source:<https://www.plumbingjohannesburg.co.za/mixing-copper-and-galvanized-pipes-is-a-bad-idea/>

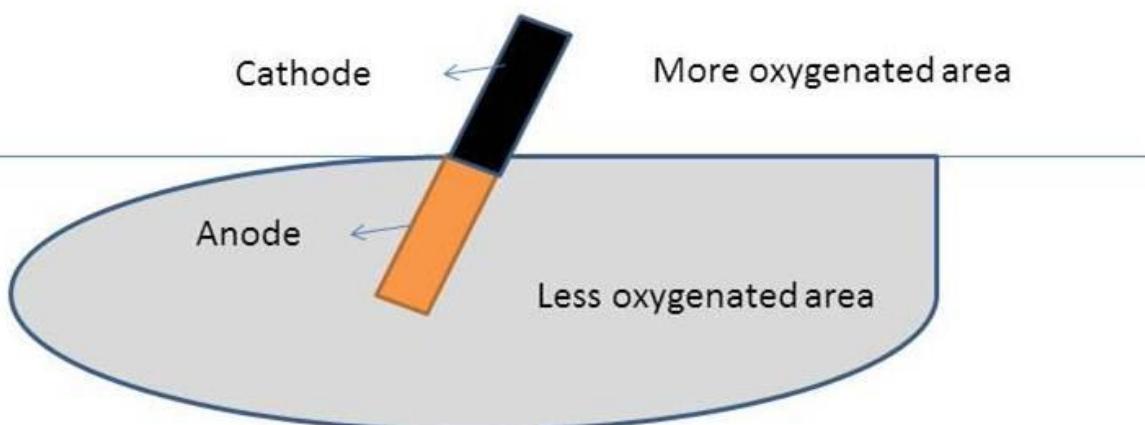
### Differential aeration corrosion:

- When a metal is exposed to **different concentrations of air ( $O_2$ )**, part of the metal exposed to **lower concentration of  $O_2$  becomes anodic** and undergoes corrosion
- Other part of the metal exposed to **higher concentration of oxygen becomes cathodic** and remains unaffected
- The difference in oxygen concentration produces a potential difference and cause corrosion current to flow

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

### Reactions:



Source:<https://chembldeacet.wordpress.com/2018/09/01/differential-aeration-corrosion/>

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---

### Examples:

- Nail from a wall



Source:<https://www.houzz.com/discussions/4120639/nails-rusted-within-the-wall>

- Wire mesh



Source:<https://www.pixtastock.com/photo/46177070>

- Paper pin inside a paper

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---



### *Class content:*

- *Types of electrochemical corrosion*
  - *Waterline corrosion*
  - *Pitting corrosion*

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---

### Waterline corrosion:

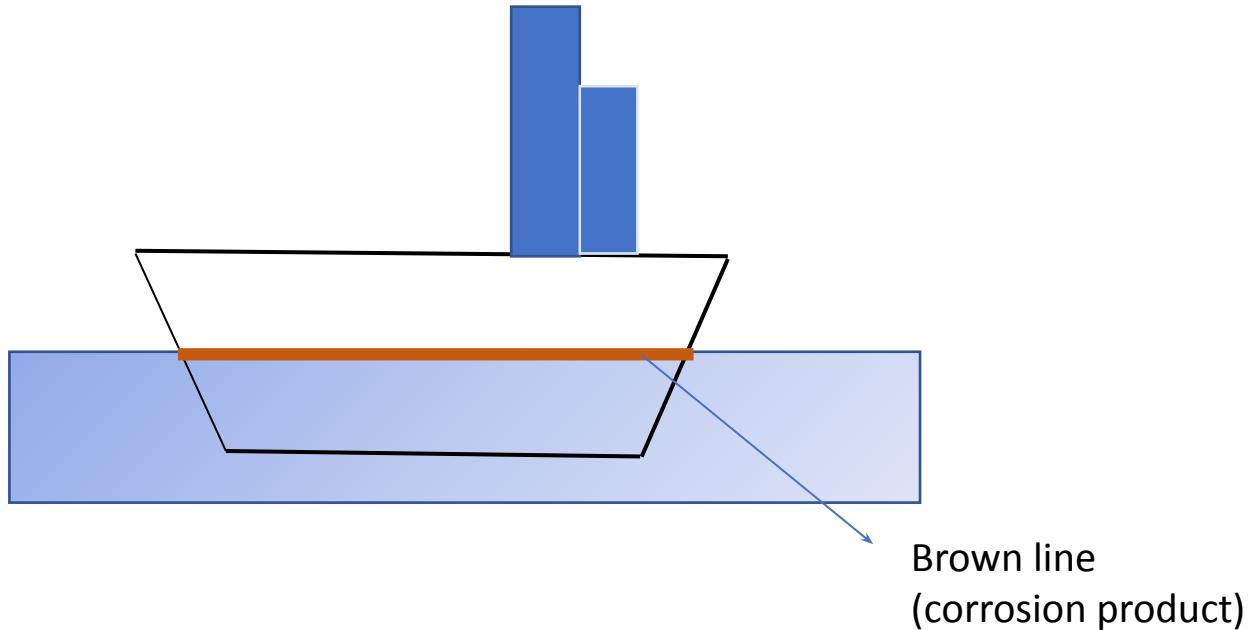
- A special case of **differential aeration corrosion**
- Observed when metal is **half immersed in water**
- The part **immersed in water** is exposed to less  $O_2$ , hence acts as anode and **gets corroded** while the **part not in water** is exposed to more  $O_2$  and acts as **cathode**; **remains unaffected** by corrosion

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

### Examples:

- Ship sailing in the sea or docked in the yard for a long time

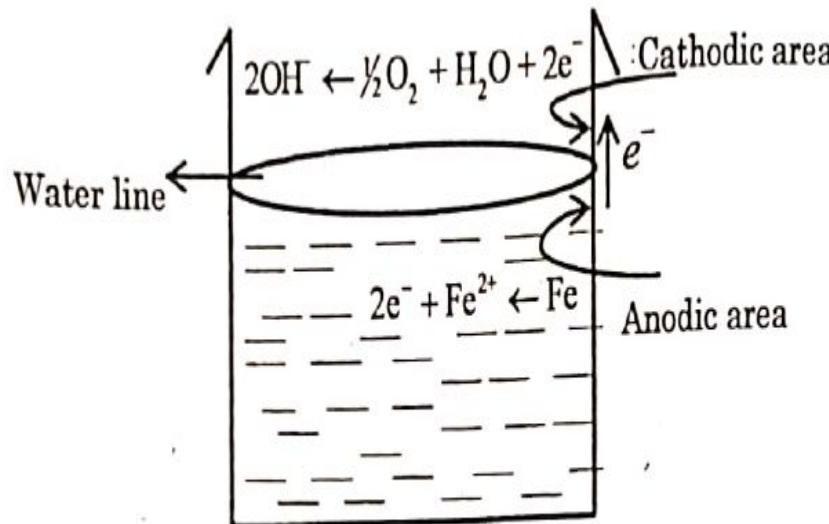


A **distinct brown line** is formed just below the water line due to the deposition of rust

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

- A steel tank is partially filled with water for a long time



Source: Basuchandra's Engineering chemistry, Banbayalu (2014)

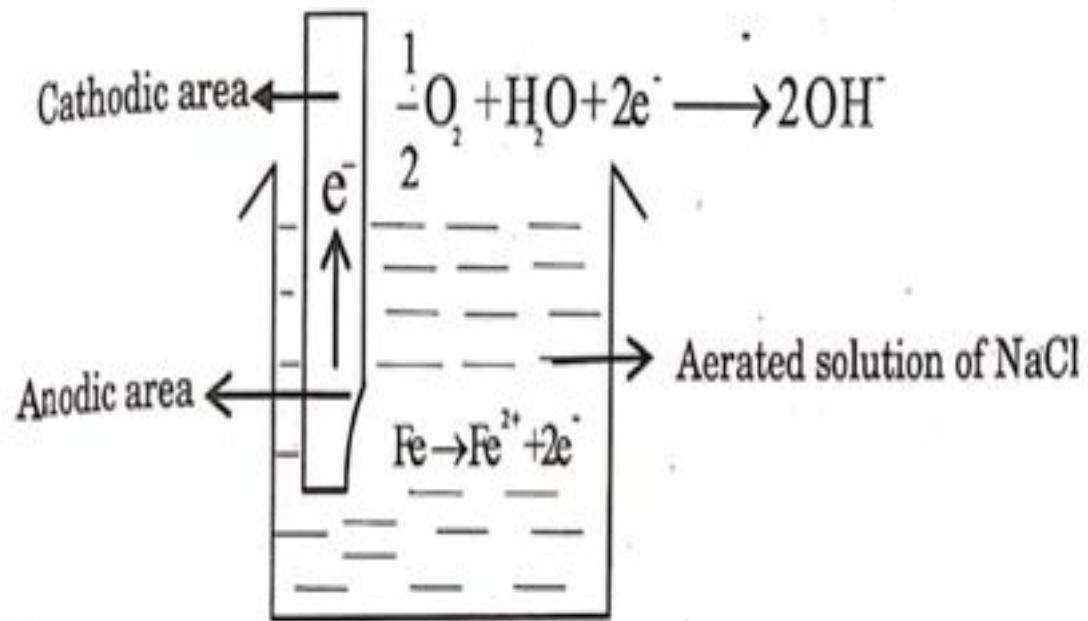
Water line corrosion

- The portion below the water line acts as anode and undergoes corrosion. The upper portion acts as cathode and remains unaffected

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

- Iron rod partially dipped in NaCl solution



Source: Basuchandra's Engineering chemistry, Banbayalu (2014)

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---

### Pitting Corrosion:

- A **localized and accelerated corrosion**
- Results in formation of **pits or pin holes**, around which the metal is relatively unattacked
- One of the most **destructive** forms of corrosion
- Characterized by **small anodic area and large cathodic area** resulting in accelerated corrosion at the anodic area



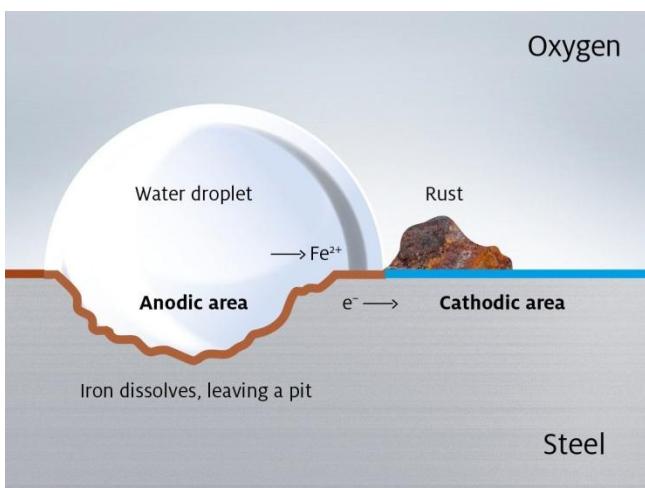
<https://www.nuflowmidwest.com/2-types-of-corrosion-that-occur-in-industrial-piping-systems/>

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

- Case 1

- When **dust particles or oil drops** get deposited over the metal surface
- The portion of the metal **covered by dust which is less aerated becomes anodic**
- The adjacent area of the metal **which is exposed to higher concentration of O<sub>2</sub>** becomes cathodic

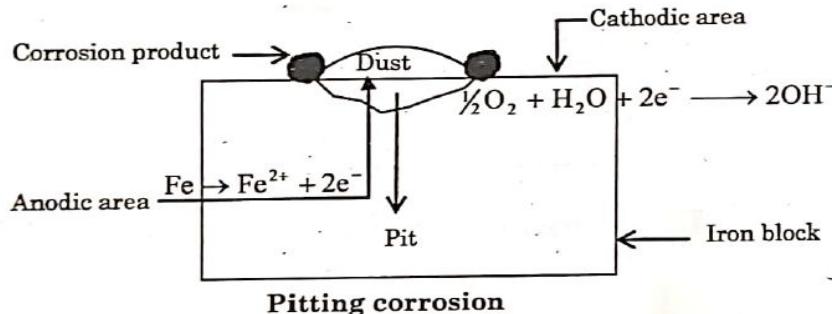


<https://www.bonderite.com/en/technologies/pretreatment/corrosion-protection.html>

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

- A small anodic region surrounded by a large cathodic region is formed
  - The demand for electrons is high from the cathode
  - Metal underneath the surface of dust particle being anode undergoes accelerated corrosion forming a deep and narrow pit
- Reactions:



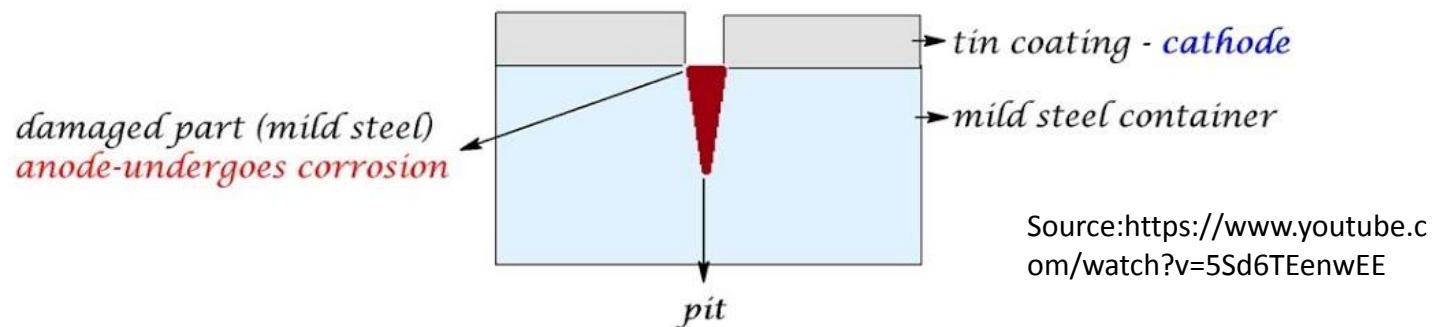
Source: Basuchandra's Engineering chemistry, Banbayalu (2014)

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

- Case II

- The **break down of the protective film** on a metal surface
- Peeling off of a small **tin coating on iron** gives rise to a small anodic area (Fe) and large cathodic area (Sn)



Source:<https://www.youtube.com/watch?v=5Sd6TEenwEE>

### Reactions:





**THANK YOU**

---

**Asha A**

Department of Science and Humanities



# ENGINEERING CHEMISTRY

---

**Asha A**

Department of Science and Humanities

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---

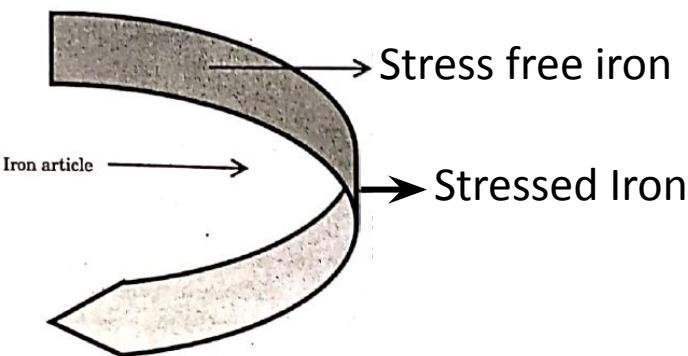


### *Class content:*

- *Types of electrochemical corrosion*
  - *Stress corrosion*
    - *Caustic embrittlement*
- *Factors affecting rate of corrosion*

### Stress Corrosion:

- Also called **Stress Corrosion Cracking**(SCC)
- A type of corrosion that occurs when some part of the metallic material is **under stress** and exposed to **specific corrosive environment**
- During the manufacture or fabrication of the articles, when the metals are subjected to **mechanical operations** such as pressing, hammering, rolling, bending, quenching, welding and riveting
- The stress can be **external stress** acting on the metal during service conditions **or residual stress or both**

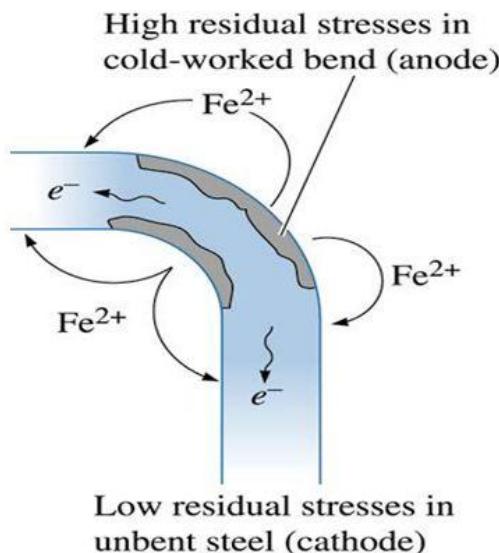


Source: Basuchandra's Engineering chemistry, Banbayalu (2014)

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

- Due to stress a **crack is initiated**
- The metal atoms under stress are always at **higher energy levels** therefore becomes **more reactive** than the stress free part
- As a result, a corrosion cell is formed with the **stressed part acting as anode** and the **stress free part acting as cathode**



Source: <https://slideplayer.com/slide/8594552/>

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---

- Conditions for stress corrosion:

- Tensile stress
- Specific corrosive environment

- Under specific corrosive environment the stressed part undergoes corrosion
- The crack deepens and results in the breakdown of the structure

- Specific corrosive environment :

- Brass - ammoniacal solution or ammonia vapours
- Steel – NaOH and chloride ions

- Causes serious damage – air crashes, bridge collapses, boiler explosions

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---

### Caustic embrittlement of boilers:



- A **form of stress corrosion** that takes place in **boilers operating at high temperature and pressure**, at the stressed regions of the boilers like rivets, joints etc.
- Water boilers made of **mild steel** undergo corrosion at the stressed portion when exposed to **concentrated alkali**

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---

- **Corrosion mechanism in water boilers:**

- When water is boiled,  $\text{Na}_2\text{CO}_3$  present in boiler water is **hydrolysed** at high temperature to give  $\text{NaOH}$
- $\text{NaOH}$  thus formed, enters the fine hair line cracks that may be present at the stressed portion of the boiler through capillary action
- Due to the high temperature,  $\text{NaOH}$  gets **concentrated** and when concentration of  $\text{NaOH}$  reaches **10 %**, it **dissolves the Iron** around it
$$2\text{NaOH} + \text{Fe} \rightarrow \text{Na}_2\text{FeO}_2 + \text{H}_2$$
- The product **sodium ferroate**( $\text{Na}_2\text{FeO}_2$ )undergoes further hydrolysis **regenerating  $\text{NaOH}$**  and  $\text{Fe}_3\text{O}_4$  is produced which is **brittle** in nature
$$3\text{Na}_2\text{FeO}_2 + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2 + 6\text{NaOH}$$

# ENGINEERING CHEMISTRY

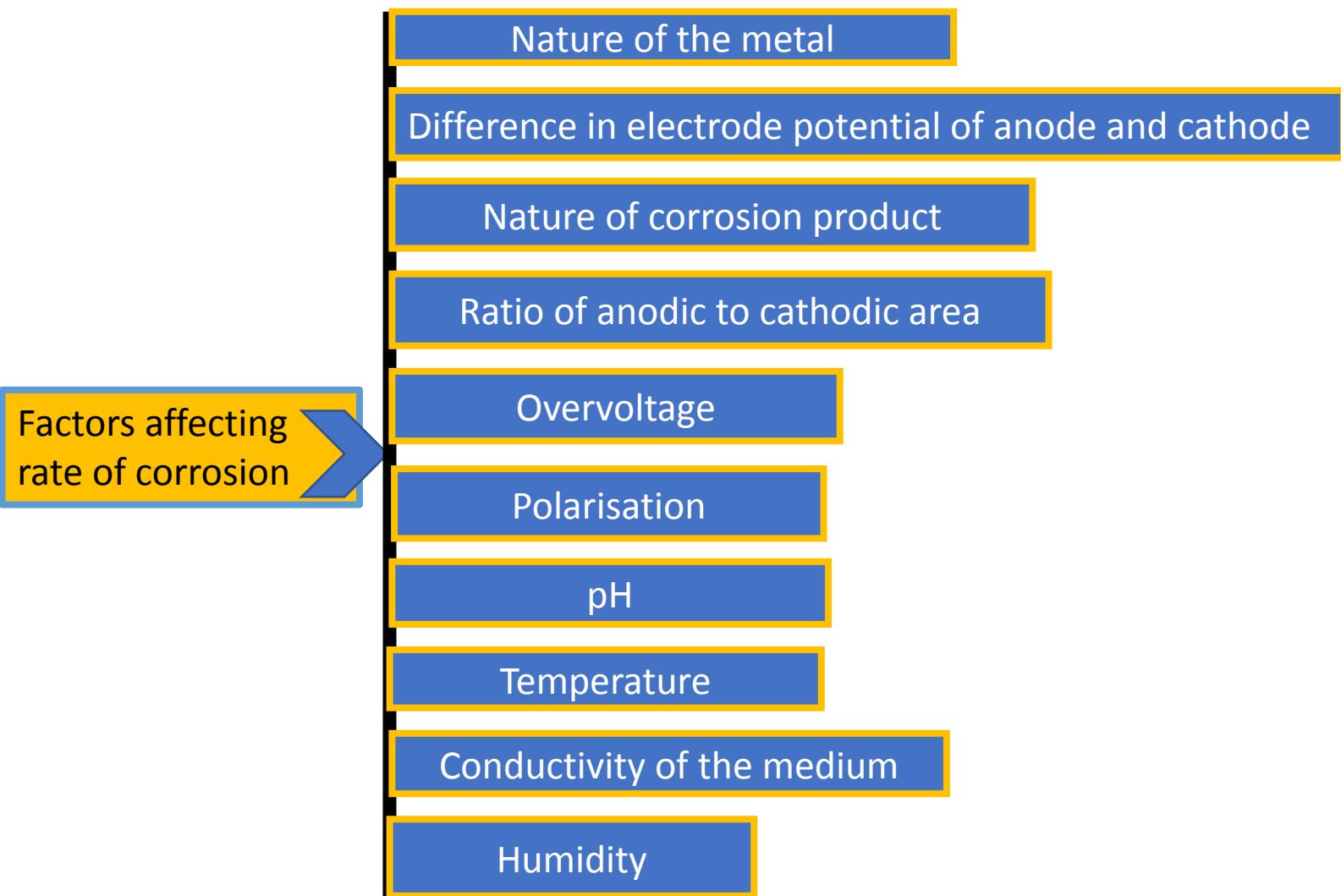
## Module 6- Corrosion Chemistry

---

- Cracks propagate along **intergranular path** which sometimes results in **explosion of the boiler**
- Since concentrated caustic soda is recognized as the specific environment required for stress corrosion of water boiler, this type of corrosion is called as **caustic embrittlement**
- The corrosion cell can be represented as follows:  
**Fe under stress (Anode)/Concentrated NaOH/Dilute NaOH/Fe stress free (Cathode)**
- Can be **prevented** by the addition of **corrosion inhibitors** such as **sodium sulfate, tannin, lignin, phosphates etc.**

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry



# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---

### Nature of the metal:

- Metals with lower electrode potential values are more reactive than the metals with higher electrode potential values
- More reactive metals are more susceptible to corrosion
- Metals like K, Na, Mg, Zn etc., with low electrode potential values are highly susceptible for corrosion
- The noble metals such as silver, gold, platinum etc., with higher potential values are less susceptible for corrosion
- **Electrochemical series** should give an idea of the order in which metals undergo corrosion
- But metals like Chromium, Aluminum Titanium etc. are exceptions as they are passive
- **Galvanic series** is required which arranges metals and alloys in the order of their tendency to undergo corrosion in a particular environment

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

### Electrochemical series

Equilibrium (Oxidants $\leftrightarrow$ Reductants)	$E^\circ$ (volts)
Lithium: $\text{Li}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Li}(\text{s})$	-3.03
Potassium: $\text{K}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{K}(\text{s})$	-2.92
Calcium: $\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Ca}(\text{s})$	-2.87
Sodium: $\text{Na}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Na}(\text{s})$	-2.71
Magnesium: $\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Mg}(\text{s})$	-2.37
Aluminum: $\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \leftrightarrow \text{Al}(\text{s})$	-1.66
Zinc: $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Zn}(\text{s})$	-0.76
Iron: $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Fe}(\text{s})$	-0.44
Lead: $\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Pb}(\text{s})$	-0.13
Hydrogen: $2\text{H}^+(\text{aq}) + 2\text{e}^- \leftrightarrow \text{H}_2(\text{g})$	0.00
Copper: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Cu}(\text{s})$	+0.34
Silver: $\text{Ag}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Ag}(\text{s})$	+0.80
Gold: $\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \leftrightarrow \text{Au}(\text{s})$	+1.50

Metal Reducing Activity Increasing

Metal Oxidizing Activity Increasing

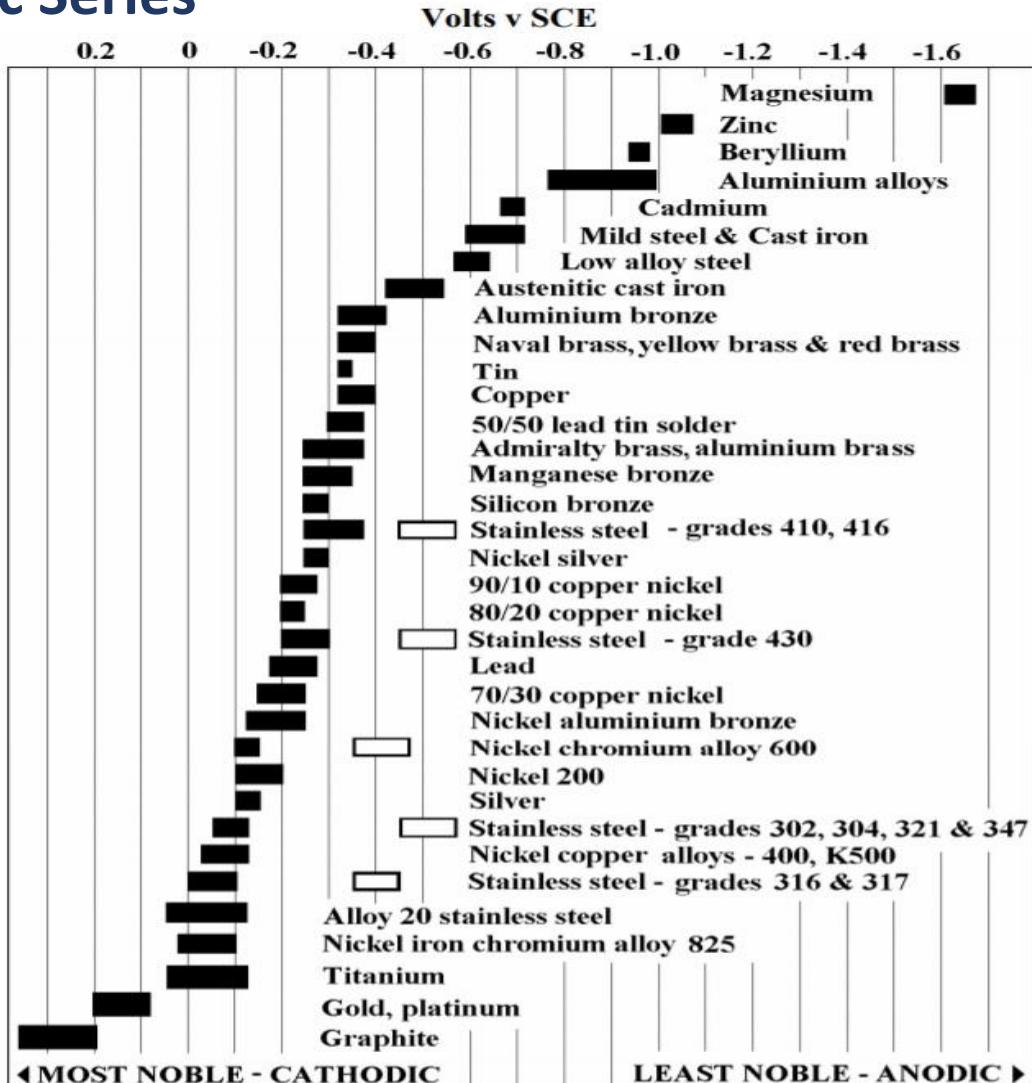
The electrochemical series is built up by arranging various redox equilibria in the order of their standard electrode potentials (redox potentials). The most negative  $E^\circ$  values are placed at the top of the electrochemical series, and the most positive at the bottom

Electrochemical series is a series of chemical elements arranged in order of their standard electrode potentials

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

### Galvanic Series



A “galvanic series” lists metal and alloys in order of their tendency to undergo corrosion in a particular electrolyte solution, hence for each specific solution which is expected to be encountered for actual use, a different order will ensue

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---

Difference in potential between anodic and cathodic region:



- Larger the potential difference between the anodic and cathodic regions, higher is the rate of galvanic corrosion
- When potential difference is more, the free energy decrease accompanying the process is higher and the corrosion rate is also higher
- Therefore when two different metals with large difference in their electrode potentials are in contact with each other, the more reactive metal undergoes corrosion very fast

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---

For example,

Case I :

Fe (-0.44V) and Cu(0.34V); the potential difference is 0.78 V

Case II

Fe(-0.44V) and Sn(-0.14V); the potential difference is 0.3 V

**Corrosion of Fe is faster when it is in contact with Cu**

- The **use of dissimilar metals** should be avoided wherever possible,e.g., **nuts and bolts** should be made of the same metal. Otherwise, the anodic metal gets corroded.

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---

### Nature of the corrosion product:

For some metals like Chromium, Aluminum etc., the **corrosion product** formed on the surface of the metal acts as a **protective film**

If the corrosion product deposited is **insoluble, stable, uniform, and non porous**, it acts as a protective film preventing further corrosion of metal

A **thin, invisible, impervious, continuous film** formed on the surface acts as a barrier between the fresh metal surface and the corrosion environment

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---

- On the other hand metals like **iron, zinc, magnesium**, etc., do not form protective film on the surface of the metal
- If the corrosion product is **soluble, unstable, non uniform, and porous**, the corrosion continues unabated
- In such cases, the fresh **metal surface is continuously exposed** to the corrosion environment and corrosion of the metal takes place continuously
- **Steel** gets corroded but **stainless steel** does not



THANK YOU

---

Asha A

Department of Science and Humanities



## ENGINEERING CHEMISTRY

---

**Asha A**

Department of Science and Humanities

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---



### *Class content:*

- *Corrosion control*
  - *Inorganic coating*
    - *Anodising*
    - *Phosphating*
  - *Organic coating*

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

### Corrosion Control

Protective  
coating

- Metallic coating
- Inorganic coating
- Organic coating

Corrosion  
Inhibitors

- Anodic Inhibitors
- Cathodic Inhibitors

Cathodic  
protection

- Sacrificial Anode method
- Impressed cathodic current method

Anodic  
Protection

- Impressed anodic current method

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---

### Protective coatings:

#### Metallic coating:

- Corrosion of base metal is prevented by coating a layer of **another metal** over it
- Metal coated may be anodic or cathodic to the base metal

#### Anodic metal coating:

Coating of a layer of metal which is anodic to base metal

e.g. , Iron article coated with Zinc

#### Cathodic metal coating:

Coating of a layer of metal which is cathodic to base metal

e.g. , Iron article coated with Tin

# Electrochemical series

Equilibrium (Oxidants $\leftrightarrow$ Reductants)	E° (volts)
Lithium: $\text{Li}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Li}(\text{s})$	-3.03
Potassium: $\text{K}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{K}(\text{s})$	-2.92
Calcium: $\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Ca}(\text{s})$	-2.87
Sodium: $\text{Na}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Na}(\text{s})$	-2.71
Magnesium: $\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Mg}(\text{s})$	-2.37
Aluminum: $\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \leftrightarrow \text{Al}(\text{s})$	-1.66
Zinc: $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Zn}(\text{s})$	-0.76
Iron: $\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Fe}(\text{s})$	-0.44
Lead: $\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Pb}(\text{s})$	-0.13
Hydrogen: $2\text{H}^+(\text{aq}) + 2\text{e}^- \leftrightarrow \text{H}_2(\text{g})$	0.00
Copper: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \leftrightarrow \text{Cu}(\text{s})$	+0.34
Silver: $\text{Ag}^+(\text{aq}) + \text{e}^- \leftrightarrow \text{Ag}(\text{s})$	+0.80
Gold: $\text{Au}^{3+}(\text{aq}) + 3\text{e}^- \leftrightarrow \text{Au}(\text{s})$	+1.50

Metal Reducing Activity Increasing

Metal Oxidizing Activity Increasing

Electrochemical series is a series of chemical elements arranged in order of their standard electrode potentials

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---



### Anodic metal coating:

Coating metal is **more active** with respect to the base metal

Even if the base metal is not completely covered, it will **not undergo pitting corrosion**

e.g., Coating of Zn or Mg on iron

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---

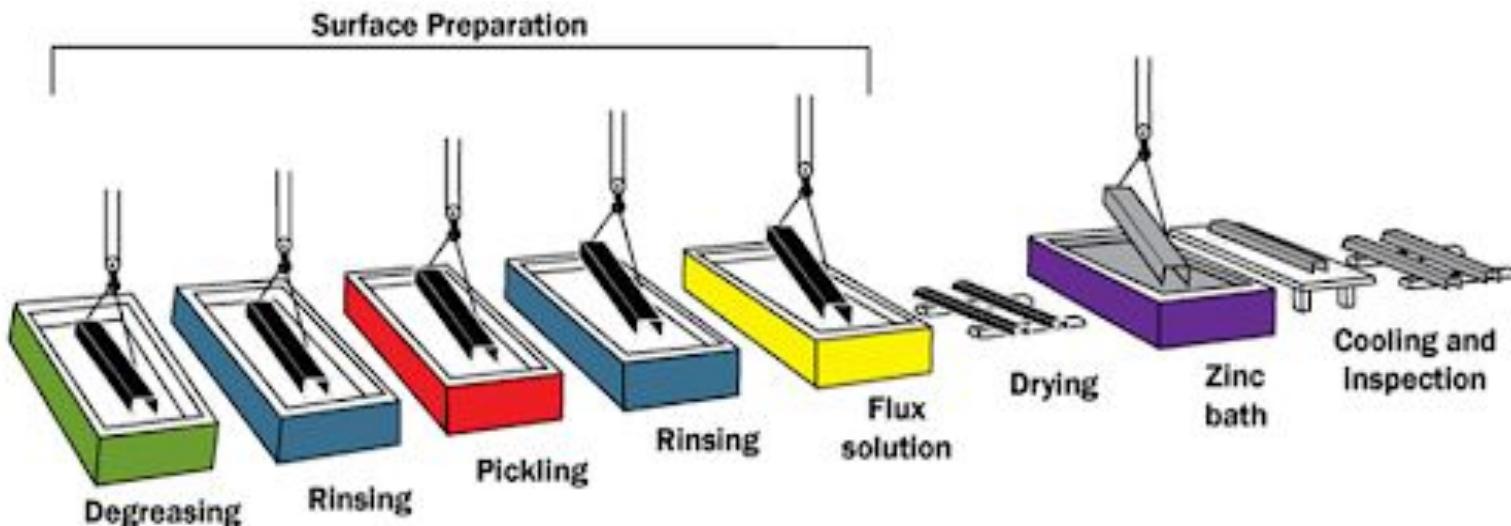
### Galvanizing:

- Coating a layer of **zinc on iron** is called galvanization
- The following steps are involved in the process:
- Iron sheet is passed through **organic solvent or caustic solution** to remove oil or grease present on it
- It is washed with **dil.  $H_2SO_4$**  to remove any rust, scale or dust present on the surface (pickling)
- It is treated with a mixture of aqueous solution of  **$ZnCl_2$  and  $NH_4Cl$**  which acts as flux which prevents oxidation and then dried
- Finally it is dipped in **molten zinc** at  $425-430^\circ C$
- **Excess zinc** present on iron sheet is removed by passing through hot rollers

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

### Process of Galvanisation



Source:<http://www.lightsoftuscany.com/faq-page/faq-galvanization.html>

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---

### Application:

Galvanization of iron is carried out to produce roofing sheets, fencing wire, buckets, bolts, nuts, pipes etc

### Advantage:

Even if the Zn coating peels off or there are gaps at some places, the **base metal (Fe) does not get corroded** because the base metal acts as cathode

### Disadvantage:

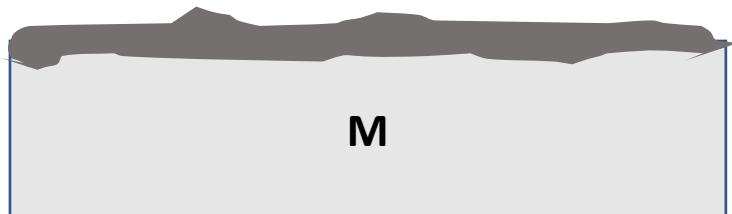
Galvanized articles are **not used for preparing and storing food** because **zinc dissolves in dilute acids** producing toxic zinc compounds

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

### Inorganic coating

- Referred to as **chemical conversion coating**
- Surface of the base metal is converted into a **protective coating** through appropriate chemical modification
- The protective film (corrosion product) is an **inherent part** of the metal



- Two methods: **Anodising and Phosphating**

# ENGINEERING CHEMISTRY

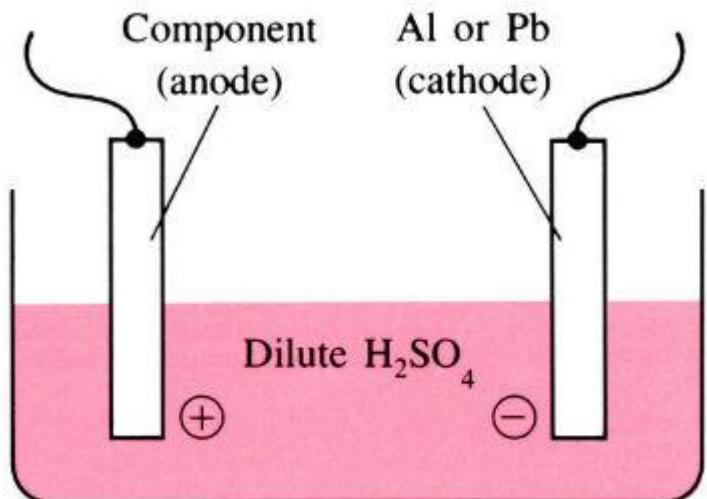
## Module 6- Corrosion Chemistry

### Anodizing:

Induced oxidation in an oxidising environment by making the article anode and passing current

Oxidation of outer layer of metal to its metal oxide which covers the metal surface and acts as protective layer

Done for non-ferrous metals like Al, Cr, Ti



Source:<https://www.open.edu/openlearn/science-maths-technology/engineering-technology/manupedia/anodising>

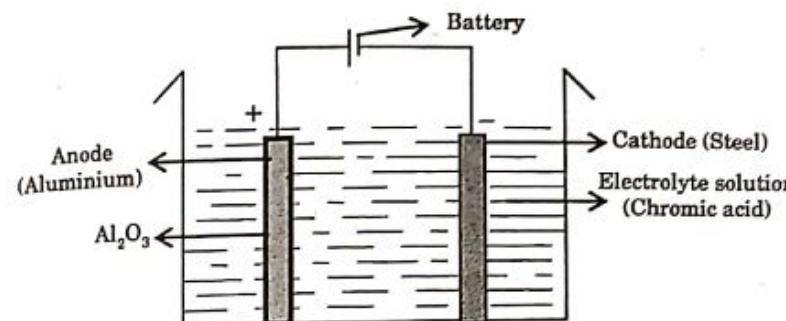
# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

### Anodizing of Aluminum:

The process:

- Article is cleaned, degreased, and polished and **taken as anode**
- It is immersed in an **electrolyte** consisting of 5-10% chromic acid, sulfuric acid, phosphoric acid, oxalic acid or their mixtures maintained at around  $40^{\circ}\text{C}$
- Lead or steel is taken as **cathode**
- **Voltage** above 40V is applied
- Outer layer of **Al is oxidised to  $\text{Al}_2\text{O}_3$**



Source: Basuchandra's Engineering chemistry,  
Banbayalu (2014)



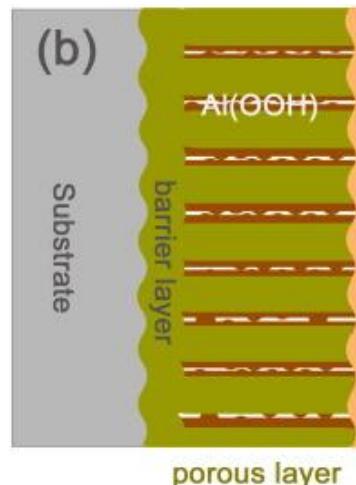
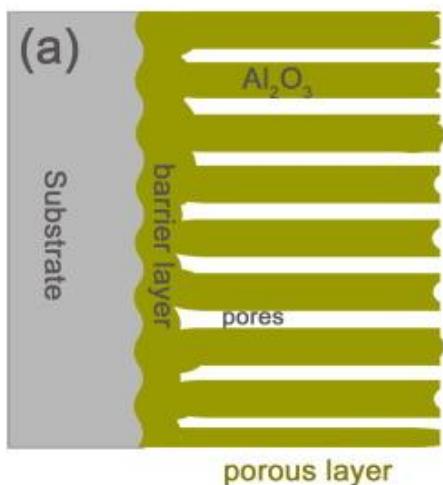
# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

$\text{Al}_2\text{O}_3$  formed on the surface is **slightly porous** in nature

The porous layer may be made compact by **sealing** which is done by immersing the anodised article in boiling water or steam

$\text{Al}_2\text{O}_3$  is converted into  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  which occupies **higher volume**; the pores are sealed



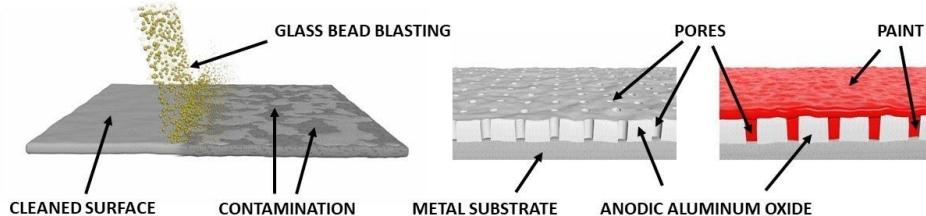
Source: <https://www.sciencedirect.com/science/article/abs/pii/S0257897215304540>

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

Anodized articles can produced in **good colour finishes** by

- Adsorbing an **organic dye** after anodising and then sealing
- Depositing a **metal like Ni, Co etc.**, into the pores



Source:<https://www.youtube.com/watch?v=w1cKVbtpe1E>

### Applications:

- Anodized Al is used as an attractive, highly durable, corrosion resistant material in exteriors for roofs, walls, buildings and also in window frames, office partitions, tiffin carriers, etc.

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---

### Phosphating:

- Converting the surface metal atoms into their **phosphates** by chemical or electrochemical reactions
- Originally phosphate coating was applied only on **Ferrous alloys** like Fe and steel. But now it has been extended, to Zn, Al and their alloys
- **Chemical phosphating** is done by dipping the article in a phosphating bath
- In **electrochemical phosphating**, the process of electrolysis is used

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---

### Chemical Phosphating:

The process -

- The phosphating bath contains three essential components:
  - **Free phosphoric acid** which reacts with the metal surface
  - **Metal phosphates** of zinc and manganese which increase adherence and decrease porosity of the coatings
  - An **accelerator** such as nitrites, chlorates, peroxides, etc. which speed up the reaction
- The process is carried out at a pH of around 3 and a temperature of 35-40°C
- The reaction include **dissolution of metal** as ions, forming a phosphate with the bath solution which subsequently gets a deposited on the surface of the metal



# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---



- Phosphate coatings are **porous** and themselves do not provide appreciable corrosion resistance
- They are useful mainly as a **base** paints and imparts good **paint adhesion** quality
- Phosphate coatings are very thin ( $3\mu\text{m}$ ) and being porous **interlock the paints** onto the surface

### Applications:

Phosphate coating is a pretreatment before painting the automobile bodies, refrigerators and washing machines

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---



### Organic coating:

- Coating of metal surfaces with **organic materials**, particularly paints and lacquers is the most widely used anti corrosion coatings
- The coatings serve to keep out air and moisture from the metal surface or serve as a **barrier** between the metal surface and the corrosion environment

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---



### *Class content:*

- *Corrosion control*
  - *Corrosion inhibitors*
    - *Anodic corrosion inhibitors*
    - *Cathodic corrosion inhibitors*

### Corrosion Inhibitors

- Chemical substances which are **added in small quantities** to the corrosive environment to decrease the rate of corrosion
- Inhibitors slow down or inhibit the **anodic or cathodic reaction** and control corrosion
- They can be used only in **confined environment**
- The action of an inhibitor depends on the **nature of the metal** to be protected as well as **corrosive environment**

- Corrosion inhibitors
- Anodic inhibitors
- Cathodic inhibitors

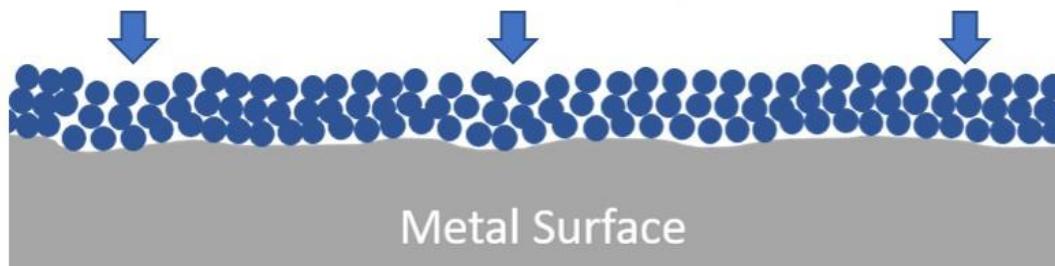
# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

### Anodic inhibitors:



- If the **formation of  $M^{n+}$**  is prevented, the corrosion process is retarded
- This is achieved by the addition of **large anions** such as chromate( $\text{CrO}_4^{2-}$ ), tungstate ( $\text{WO}_4^{2-}$ ), etc.
- These ions combine with  $M^{n+}$  and **form a precipitate** which covers the surface of the anode



Source:<http://www.penriteoil.com.au/knowledge-centre/Coolant%20Inhibitor%20Packs/149/what-are-corrosion-inhibitors/289>

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---



- Anodic inhibitors are found to be effective only when **sufficient amount** of the inhibitor is added into the corrosion medium
- If insufficient quantity is added, then a part of the anodic region is exposed to the environment
- Formation of small anodic area results in **intense corrosion**
- **Salts like  $\text{Na}_2\text{CrO}_4$ ,  $\text{Na}_2\text{WO}_4$**

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---

### Cathodic inhibitors:

- **liberation of hydrogen**
- **absorption of oxygen**
- Inhibiting any of these reactions will **slow down the cathodic reaction** which in turn slows down the anodic reaction; corrosion is inhibited

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---

Inhibition of hydrogen liberation:

Preventing the diffusion of  $H^+$  ions to the cathode-

- By the addition of certain **organic compounds** which contain **nitrogen or sulfur**
- **Aliphatic amines, urea, thiourea, mercaptans, heterocyclic compounds** are widely used as cathodic inhibitors
- They get **adsorbed on the cathodic region** forming a protective film, preventing the  $H^+$  ions from coming in contact with the cathodic metal surface

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---

By increasing the hydrogen overvoltage on the metal surface –



- When Hydrogen overvoltage is high , **liberation of H<sub>2</sub>** will be difficult
- By the addition of **oxides of arsenic, antimony**(As<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>) or salts like **sodium meta-arsenite**(NaAsO<sub>2</sub>)
  - They **deposit** on the cathode region
  - The **hydrogen overvoltage on these metals is very high**; liberation of H<sub>2</sub> is reduced

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---

Inhibition of oxygen absorption:

By removing the oxygen from the corrosive media -

- By adding **Oxygen scavengers** like hydrazine



- By adding **reducing agents** sodium sulfite etc.



# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

By decreasing the diffusion rate of oxygen to cathode –

- By adding salts with large cations such as  $\text{ZnSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{NiSO}_4$  etc.
- The **cations** of the salts ( $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ ) migrate towards the cathode surface and **react with the hydroxyl ions** formed at the cathode



- The **hydroxides get deposited** on the cathodic sites
- The **protective film** impermeable to oxygen prevents its diffusion to the cathodic region

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---



### Limitations:

- They **contaminate** the environment
- Many of the inhibitors are **toxic**, cannot be used in systems which come in contact with humans
- Can be used only in **closed systems** in which corrosive environment is either contained or re-circulated

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---



### *Class content:*

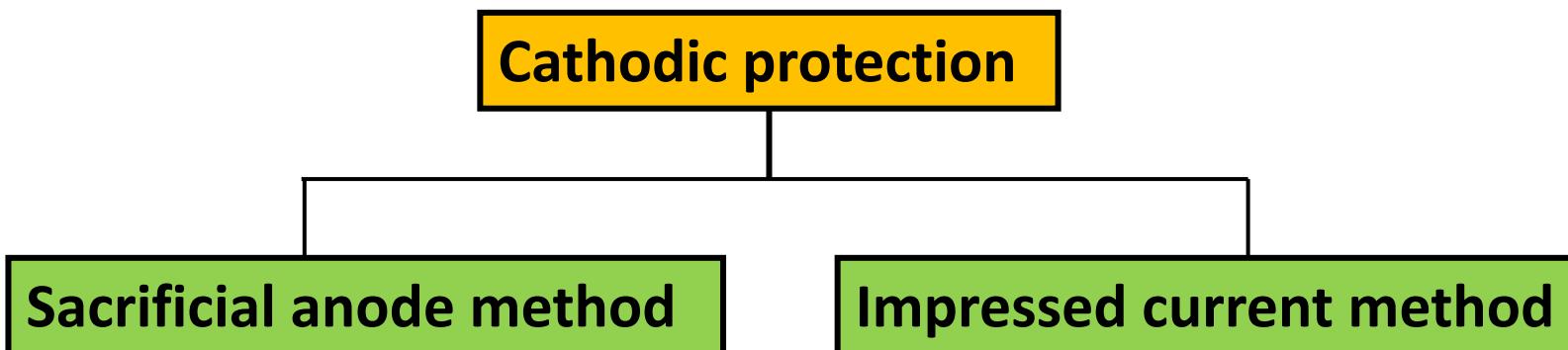
- *Corrosion control*
  - *Cathodic protection*
    - *Sacrificial anode method*
    - *Impressed cathodic current method*

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

### Cathodic protection:

- By converting it **completely into cathode** and no part of it is allowed to act as anode
- Cathode does not undergo corrosion so the structure is protected



# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---

### Sacrificial anode method:



- In this method, protected metal structure is converted into a cathode **by connecting it to a more active metal**
- This active metal (example: zinc, magnesium) acts as an **auxiliary anode**
- These metals being more active, acts as anode and undergo **preferential corrosion**, protecting the metal structure
- Since the **anodic metals are sacrificed** to protect the metal structure, the method is known as sacrificial anode method
- Exhausted anodes have to be **replaced periodically**

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

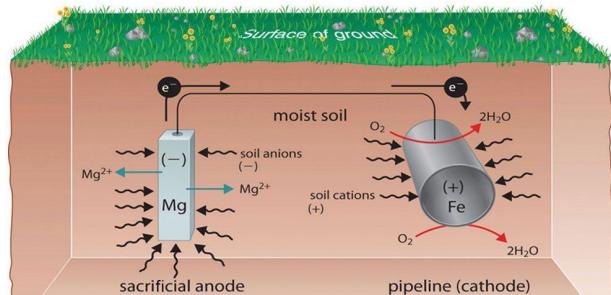
### Examples:

- **Mg/Zn bars** are fixed to the **sides of ocean going ships** to act as sacrificial anodes



Source:<https://thenavalarch.com/ship-corrosion-cathodic-protection-sacrificial-anodes/>

- **Mg/Zn blocks** are connected to **buried pipe lines**



Source:<https://www.pipelineprotection.co.uk/services/cathodic-protection/>

- A **Mg block** connected to a **buried oil storage tank**

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---



### Advantages:

- The method is simple
- Low installation cost
- Does not require power supply

### Disadvantages:

- Involves recurring expenditure for replacement of consumed anodes

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

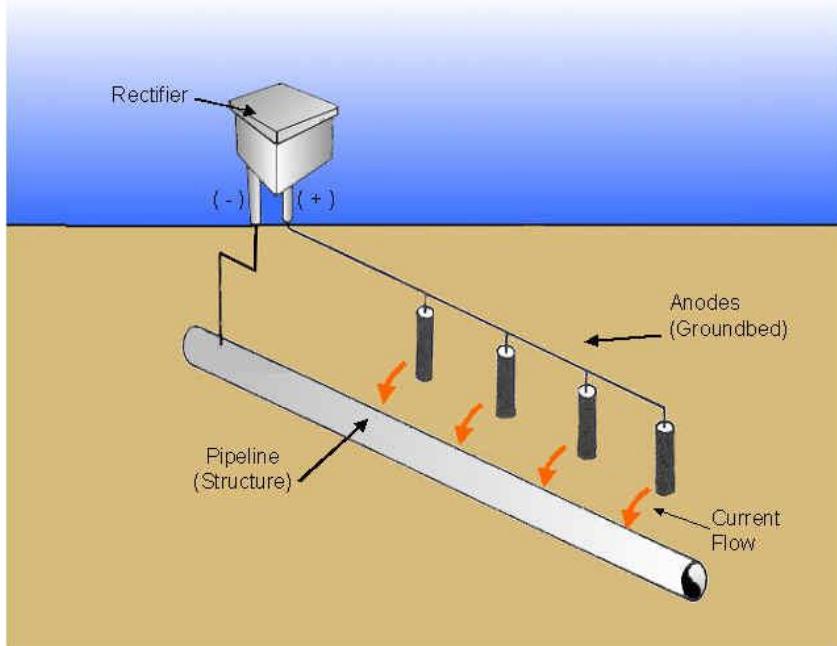
---

### Impressed current method:

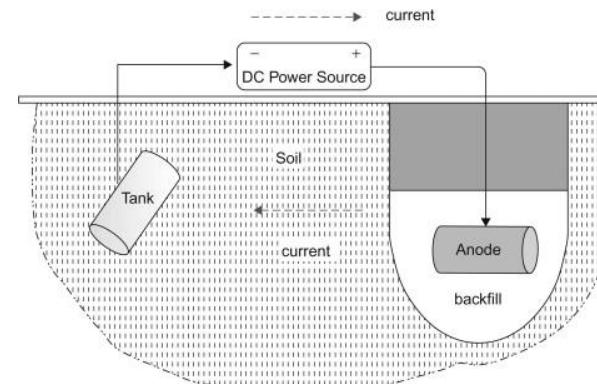
- By applying a **direct current**
- The **protected metal is made cathodic** by connecting it to the cathode of the external source of current
- Anode of the external source is usually connected to an **inert electrode** like graphite; Platinum, silicon, iron are also used as anodes
- A **backfill of coke ,bentonite** is used to improve efficiency of the anode
- The metal structure being cathode **does not undergo corrosion**
- Anode being inert remains **unaffected**

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry



Source:<https://www.mcwaneductile.com/blog/v-bio-r-or-cathodic-protection-an-honest-comparison/>



Source:<https://www.sciencedirect.com/topics/engineering/impressed-current-system>

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---



### Advantages:

- One installation can protect large area of metal

### Limitations:

- Rather expensive, since it needs **high current** for safe protection of structure
- If the impressed current is **not uniform** on the entire surface of the protected structure, **localized corrosion** takes place on the protected metal

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---



- If hydrogen liberation is the cathodic reaction on the metal surface, then the protected metal may suffer from **hydrogen embrittlement**
- **Hydrogen embrittlement:**  
 $H_2$  molecule being small **enters the metal lattice** and when the pressure increases , it **causes blisters** and makes the metal brittle

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---



### *Class content:*

- *Corrosion control*
  - *Anodic Protection*
    - *Impressed current method*

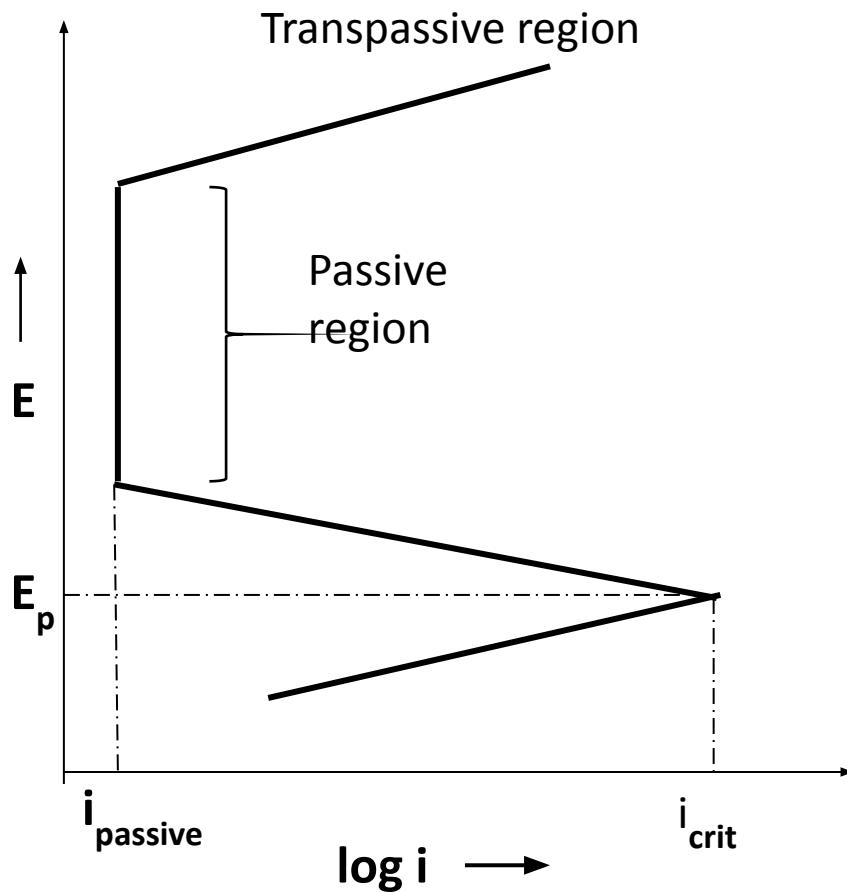
### Anodic protection:

- Prevention of corrosion by **impressed anodic current** is called as anodic protection
- The article to be protected is made **anode** by connecting it to the **anode terminal of the power source**
- Can be used only for metals which show **active-passive behaviour** like nickel, iron, chromium, titanium and their alloys
- On applying an **optimum potential** these metals get passivated and rate of corrosion decreases

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

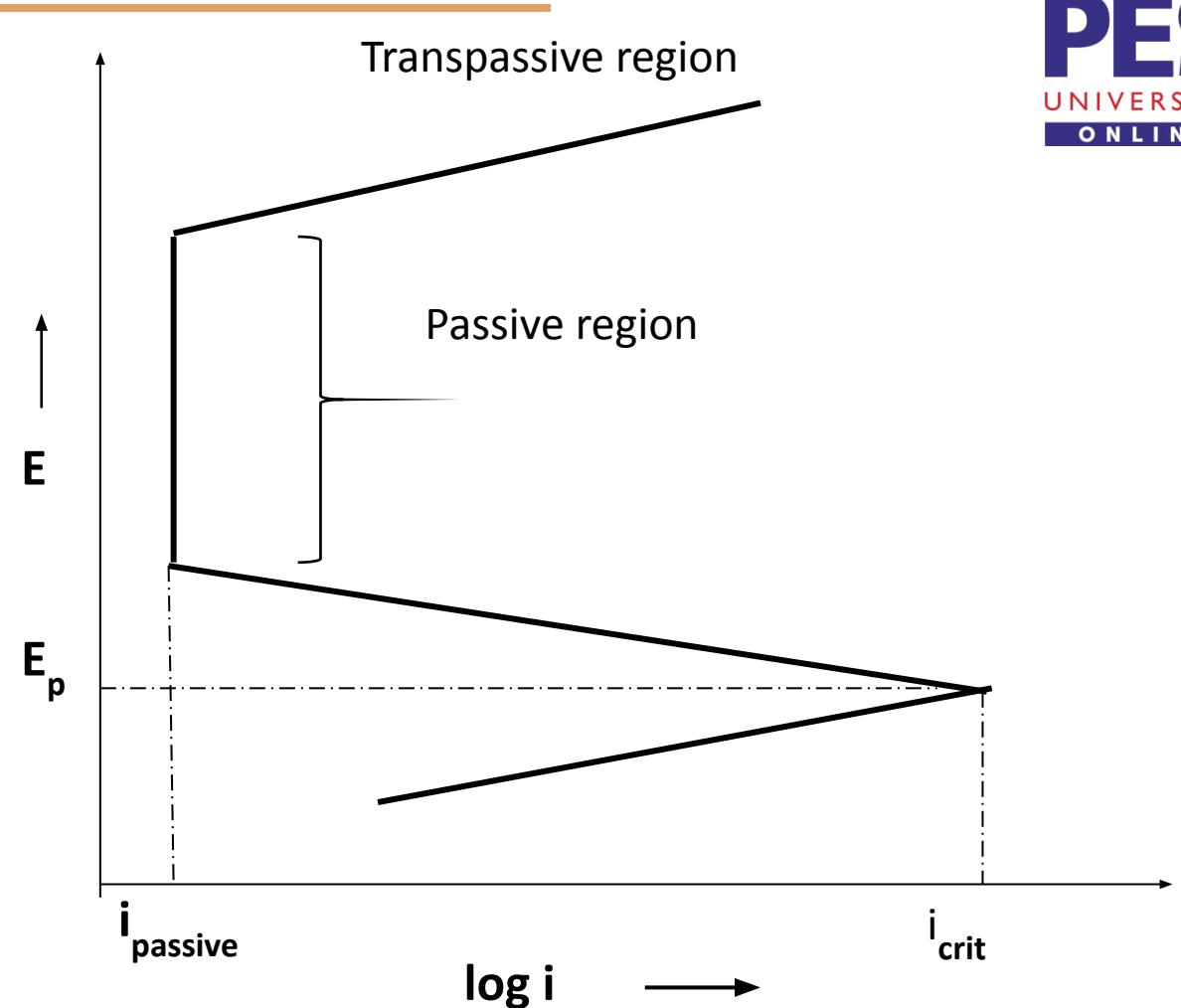
Active – passive transition of metals with the application of a potential can be explained from the potential-current curve



# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

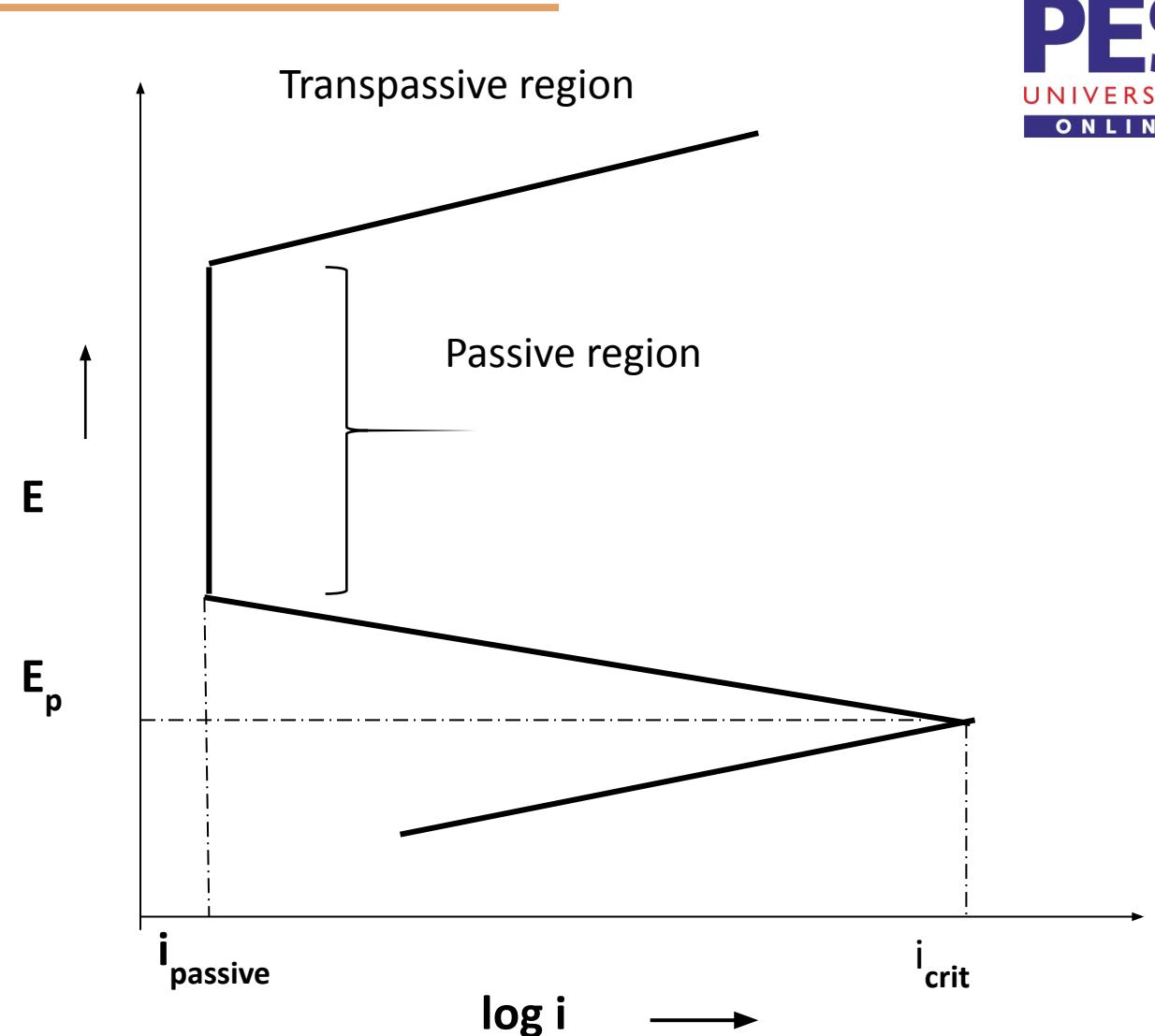
- A known **potential** is applied to the metal specimen and **current** is measured
- As the potential is increased, initially the **current also increases**, and it indicates the dissolution of metal
- This trend continues until the current reaches a **critical value ( $i_{crit}$ )** and passivation due to the development of oxide layer sets in
- The potential required for the passivation due to the development of oxide layer, this potential called **passivating potential ( $E_p$ )**



# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

- Above  $E_p$ , the current flow decreases and reaches a minimum value called **passivation current,  $i_{\text{passive}}$**
- If the potential is increased further, the metal remains unattacked up to a particular potential is reached. **In this range, corrosion rate of the metal is very small.** This potential range, in which anodic potential can be achieved, is called **passive region**
- If the potential is increased further, corrosion rate increases and this region is called the **transpassive region**
- The optimum potential for protection is determined by electrochemical measurements



# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---



Anodic protection to a structure is applied by using a device

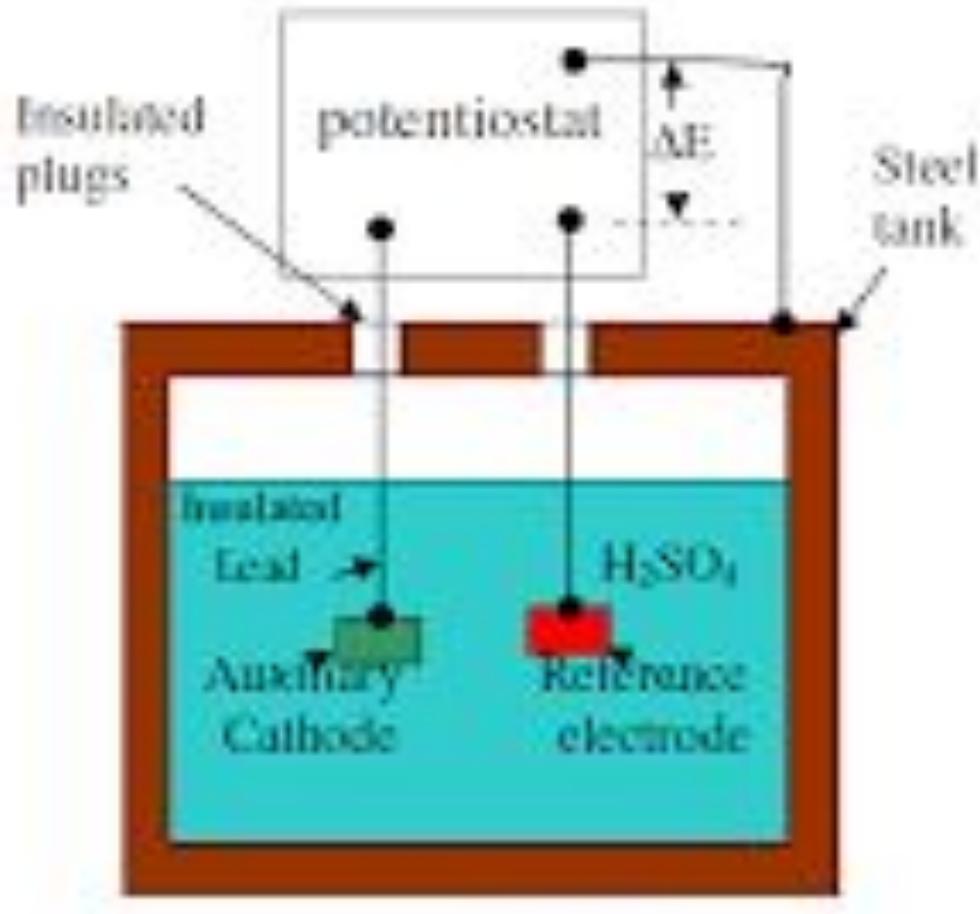
called **potentiostat**

- It is an electronic device that maintains a metal at a **constant potential with respect to a reference electrode**
- Potentiostat has **three terminals**, one connected to the anode, another to an auxillary cathode(Pt) and the third connected to a reference electrode

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

Anodic protection of a steel tank carrying  $H_2SO_4$



- One terminal is connected to the storage tank(anode)
- Other is connected to the reference electrode and a constant potential corresponding to the passive range is maintained between tank and the reference electrode
- The third terminal is connected to an auxiliary electrode like Pt

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---



### Advantages:

- Applicability in extremely corrosive environments
- Low current demand

### Disadvantages:

- Restricted to metals that show active-passive behaviour
- Initial installation cost is high
- Cannot reduce corrosion rate to zero unlike cathodic protection



THANK YOU

---

Asha A

Department of Science and Humanities



# ENGINEERING CHEMISTRY

---

**Asha A**

Department of Science and Humanities

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---



### *Class content:*

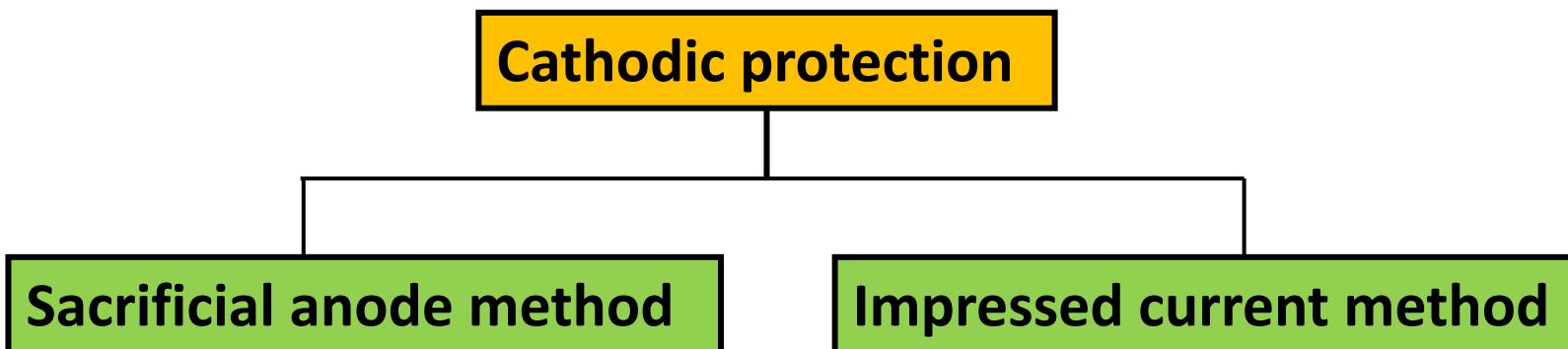
- *Corrosion control*
  - *Cathodic protection*
    - *Sacrificial anode method*
    - *Impressed cathodic current method*

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

### Cathodic protection:

- By converting it **completely into cathode** and no part of it is allowed to act as anode
- Cathode does not undergo corrosion so the structure is protected



# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---

### Sacrificial anode method:



- In this method, protected metal structure is converted into a cathode **by connecting it to a more active metal**
- This active metal (example: zinc, magnesium) acts as an **auxiliary anode**
- These metals being more active, acts as anode and undergo **preferential corrosion**, protecting the metal structure
- Since the **anodic metals are sacrificed** to protect the metal structure, the method is known as sacrificial anode method
- Exhausted anodes have to be **replaced periodically**

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

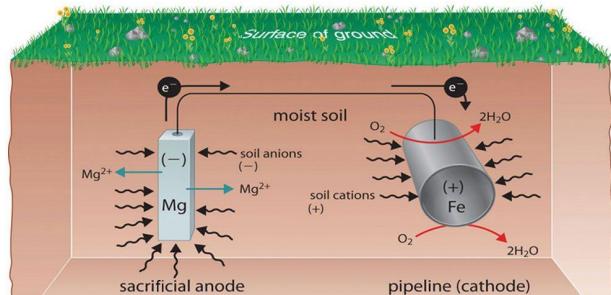
### Examples:

- Mg/Zn bars are fixed to the **sides of ocean going ships** to act as sacrificial anodes



Source:<https://thenavalarch.com/ship-corrosion-cathodic-protection-sacrificial-anodes/>

- Mg/Zn blocks are connected to **buried pipe lines**



Source:<https://www.pipelineprotection.co.uk/services/cathodic-protection/>

- A Mg block connected to a **buried oil storage tank**

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---



### Advantages:

- The method is simple
- Low installation cost
- Does not require power supply

### Disadvantages:

- Involves recurring expenditure for replacement of consumed anodes

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

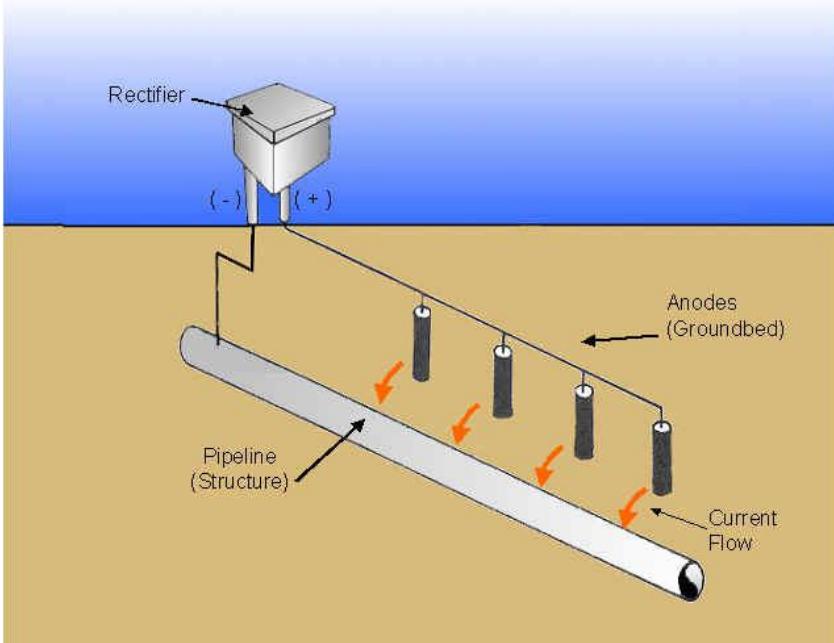
---

### Impressed current method:

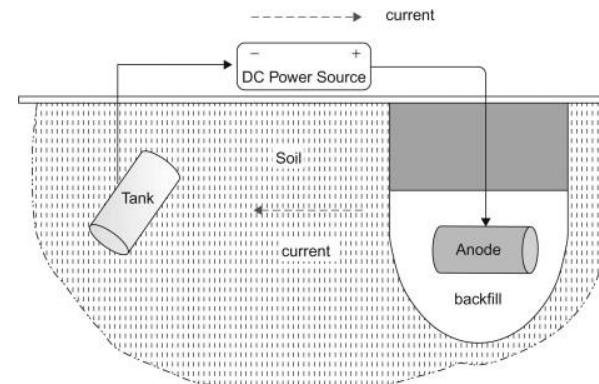
- By applying a **direct current**
- The **protected metal is made cathodic** by connecting it to the cathode of the external source of current
- Anode of the external source is usually connected to an **inert electrode** like graphite; Platinum, silicon, iron are also used as anodes
- A **backfill of coke ,bentonite** is used to improve efficiency of the anode
- The metal structure being cathode **does not undergo corrosion**
- Anode being inert remains **unaffected**

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry



Source:<https://www.mcwaneductile.com/blog/v-bio-r-or-cathodic-protection-an-honest-comparison/>



Source:<https://www.sciencedirect.com/topics/engineering/impressed-current-system>

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---



### Advantages:

- One installation can protect large area of metal

### Limitations:

- Rather expensive, since it needs **high current** for safe protection of structure
- If the impressed current is **not uniform** on the entire surface of the protected structure, **localized corrosion** takes place on the protected metal

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---



- If hydrogen liberation is the cathodic reaction on the metal surface, then the protected metal may suffer from **hydrogen embrittlement**
- **Hydrogen embrittlement:**  
 $H_2$  molecule being small **enters the metal lattice** and when the pressure increases , it **causes blisters** and makes the metal brittle

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---



### *Class content:*

- *Corrosion control*
  - *Anodic Protection*
    - *Impressed current method*

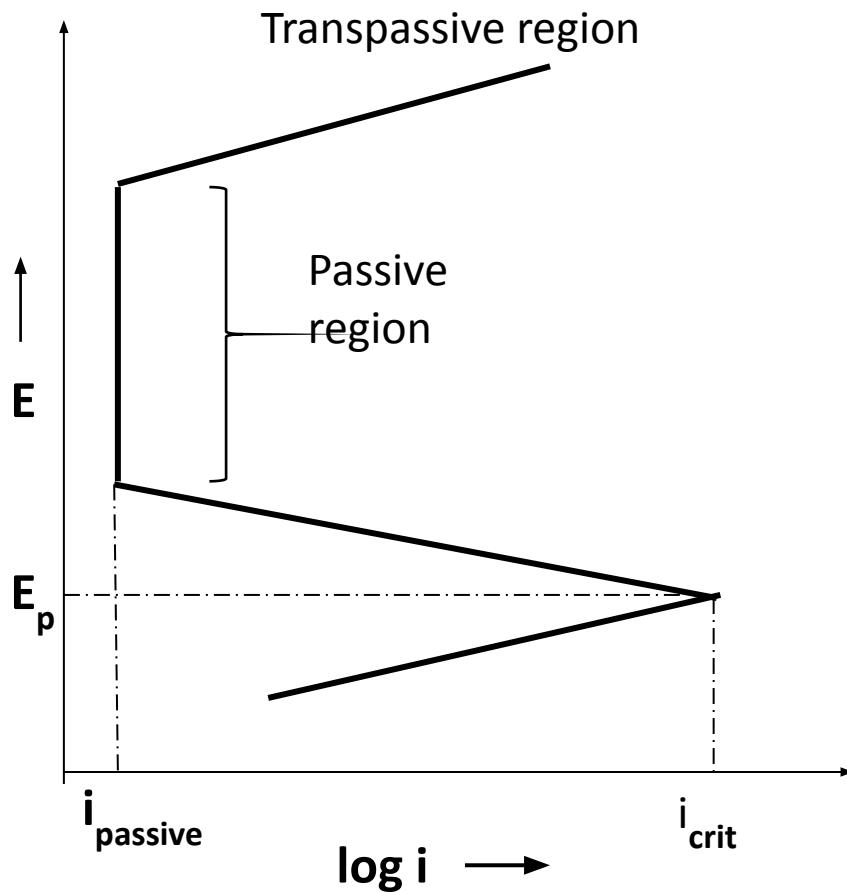
### Anodic protection:

- Prevention of corrosion by **impressed anodic current** is called as anodic protection
- The article to be protected is made **anode** by connecting it to the **anode terminal of the power source**
- Can be used only for metals which show **active-passive behaviour** like nickel, iron, chromium, titanium and their alloys
- On applying an **optimum potential** these metals get passivated and rate of corrosion decreases

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

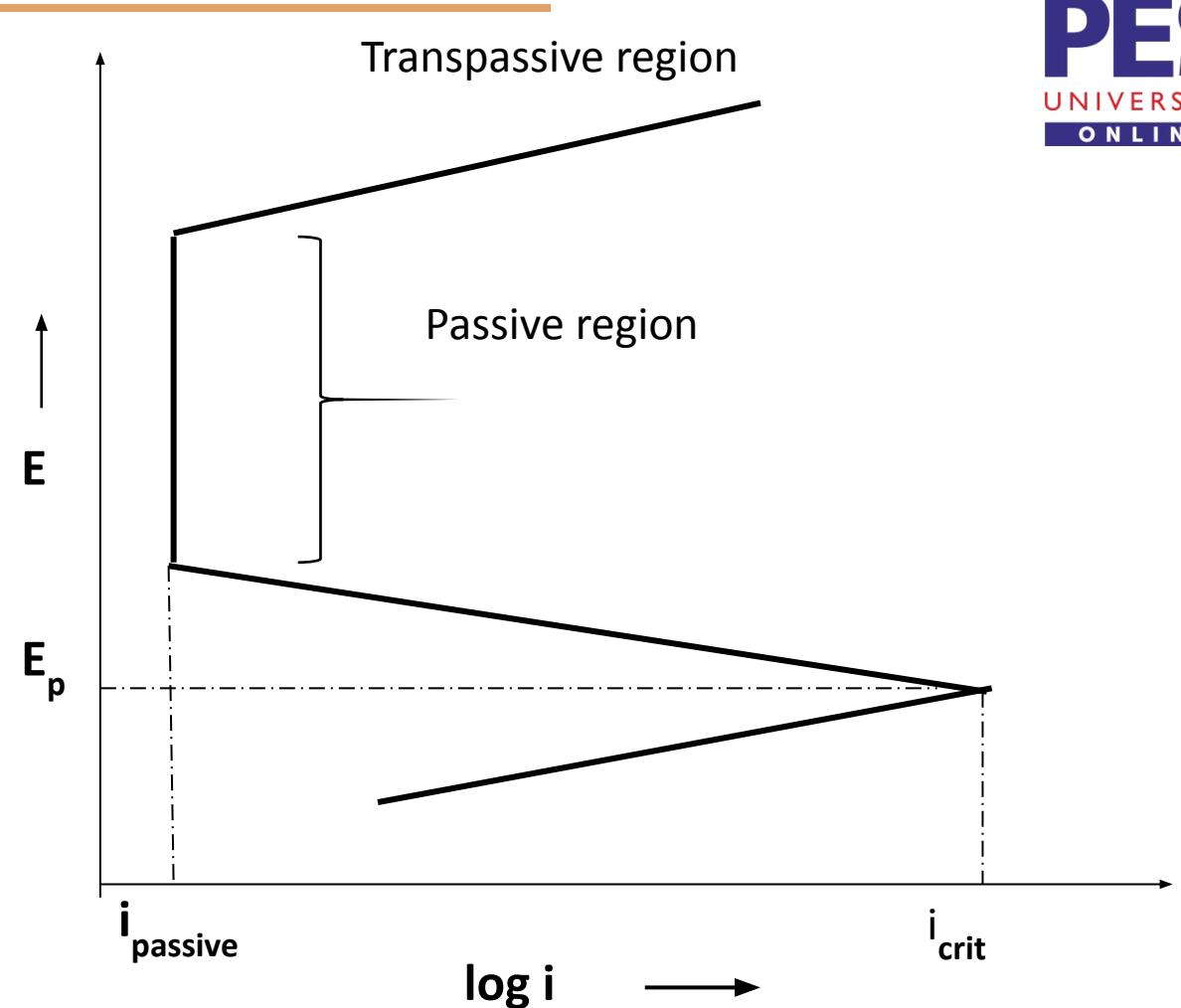
Active – passive transition of metals with the application of a potential can be explained from the potential-current curve



# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

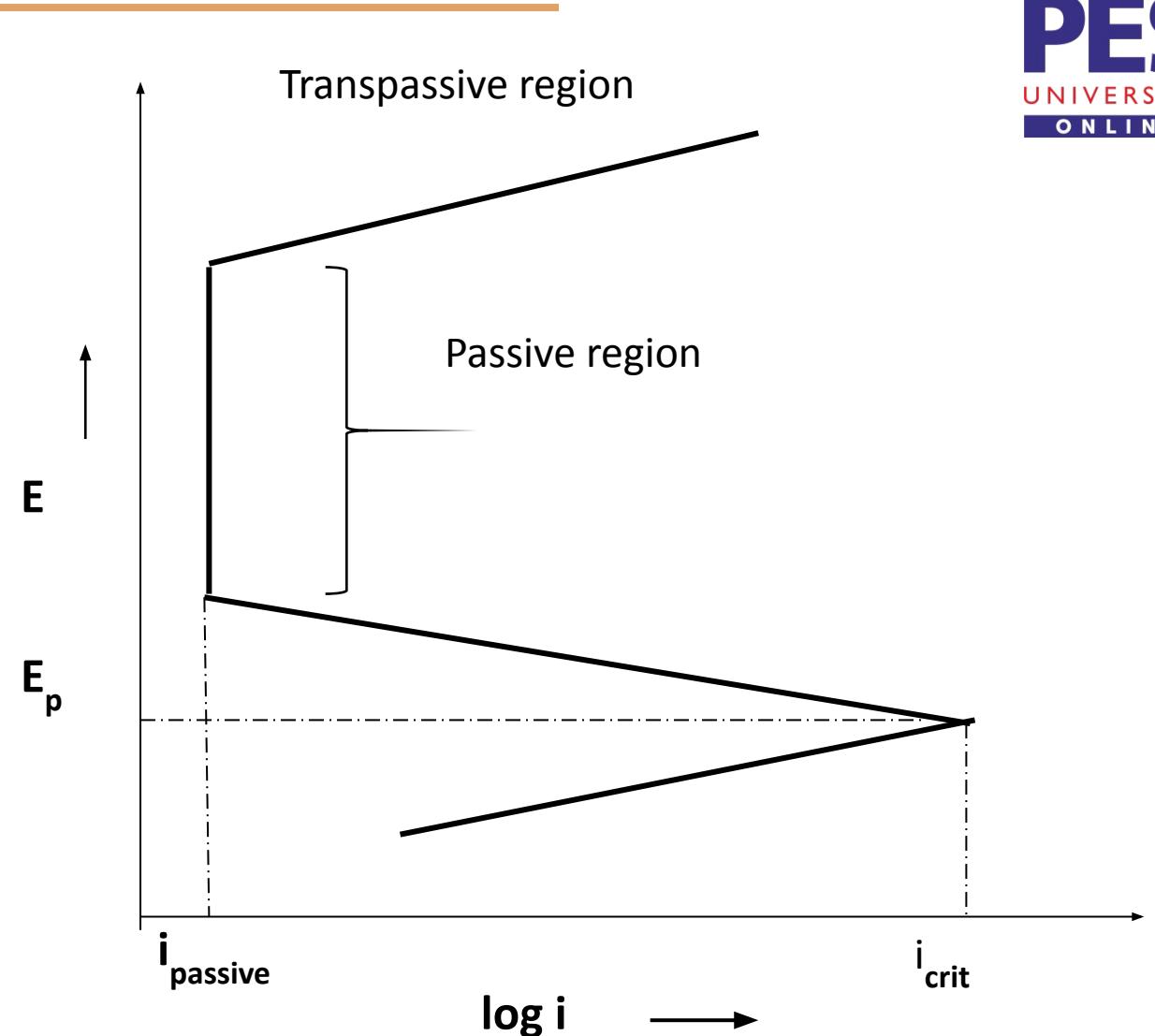
- A known **potential** is applied to the metal specimen and **current** is measured
- As the potential is increased, initially the **current also increases**, and it indicates the dissolution of metal
- This trend continues until the current reaches a **critical value ( $i_{crit}$ )** and passivation due to the development of oxide layer sets in
- The potential required for the passivation due to the development of oxide layer, this potential called **passivating potential ( $E_p$ )**



# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

- Above  $E_p$ , the current flow decreases and reaches a minimum value called **passivation current,  $i_{\text{passive}}$**
- If the potential is increased further, the metal remains unattacked up to a particular potential is reached. **In this range, corrosion rate of the metal is very small.** This potential range, in which anodic potential can be achieved, is called **passive region**
- If the potential is increased further, corrosion rate increases and this region is called the **transpassive region**
- The optimum potential for protection is determined by electrochemical measurements



# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---



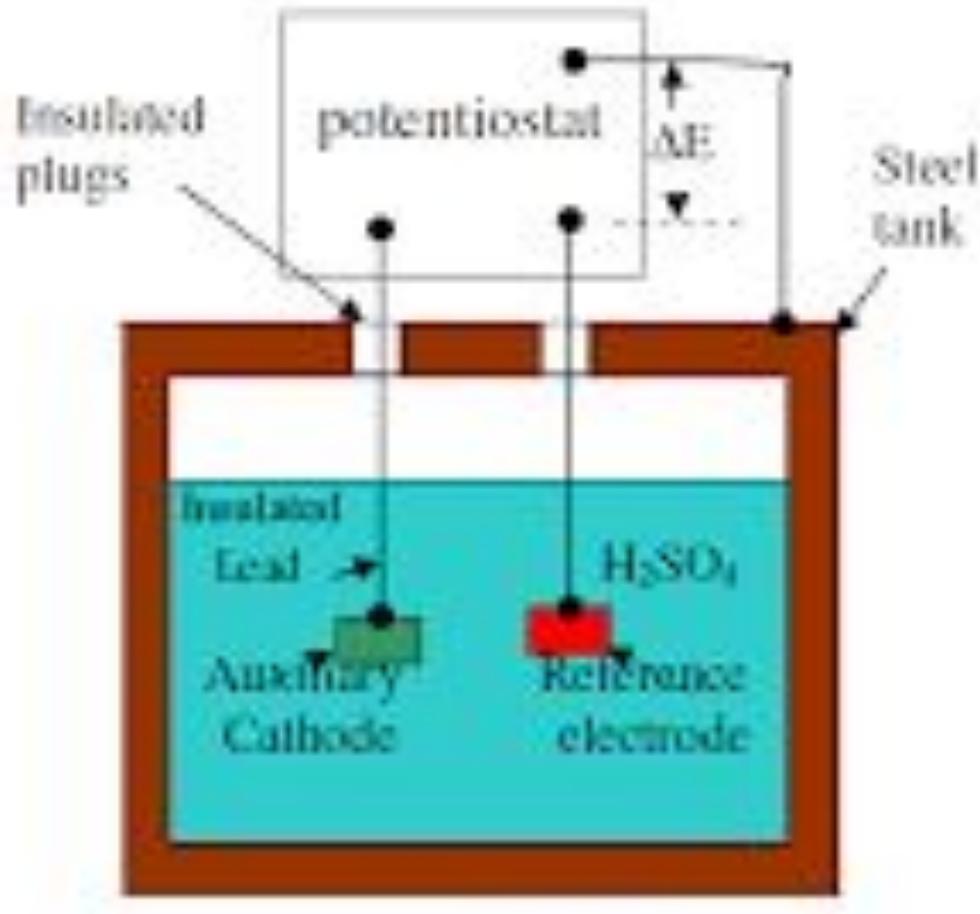
Anodic protection to a structure is applied by using a device called **potentiostat**

- It is an electronic device that maintains a metal at a **constant potential with respect to a reference electrode**
- Potentiostat has **three terminals**, one connected to the anode, another to an auxillary cathode(Pt) and the third connected to a reference electrode

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

Anodic protection of a steel tank carrying  $H_2SO_4$



- One terminal is connected to the storage tank(anode)
- Other is connected to the reference electrode and a constant potential corresponding to the passive range is maintained between tank and the reference electrode
- The third terminal is connected to an auxiliary electrode like Pt

# ENGINEERING CHEMISTRY

## Module 6- Corrosion Chemistry

---



### Advantages:

- Applicability in extremely corrosive environments
- Low current demand

### Disadvantages:

- Restricted to metals that show active-passive behaviour
- Initial installation cost is high
- Cannot reduce corrosion rate to zero unlike cathodic protection



**THANK YOU**

---

**Asha A**

Department of Science and Humanities