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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*

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Module 1- Electrochemical equilibria



Class content:

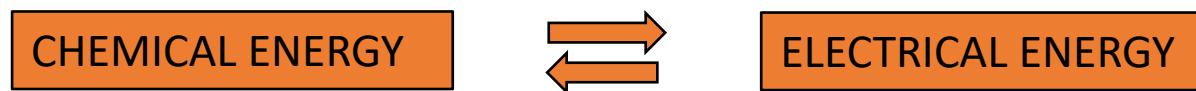
- *Origin of electrode potential*
- *Cell potential*
- *Nernst Equation*

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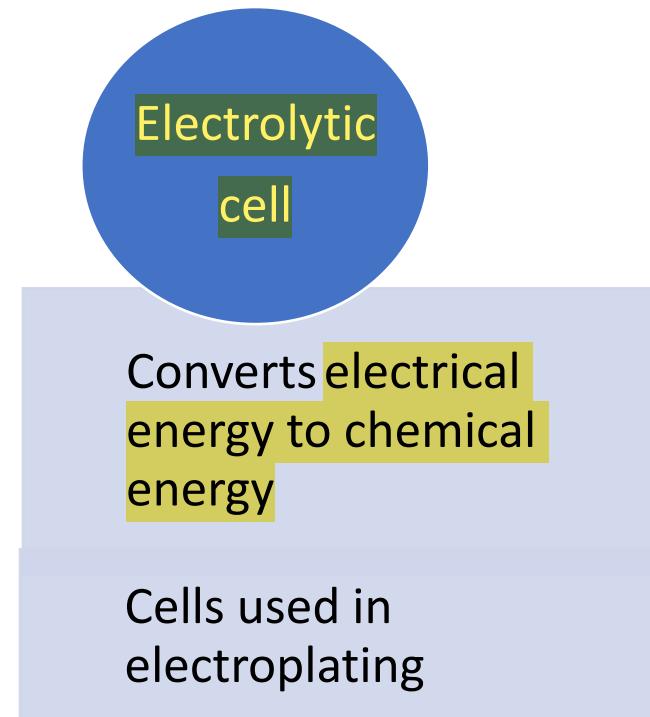
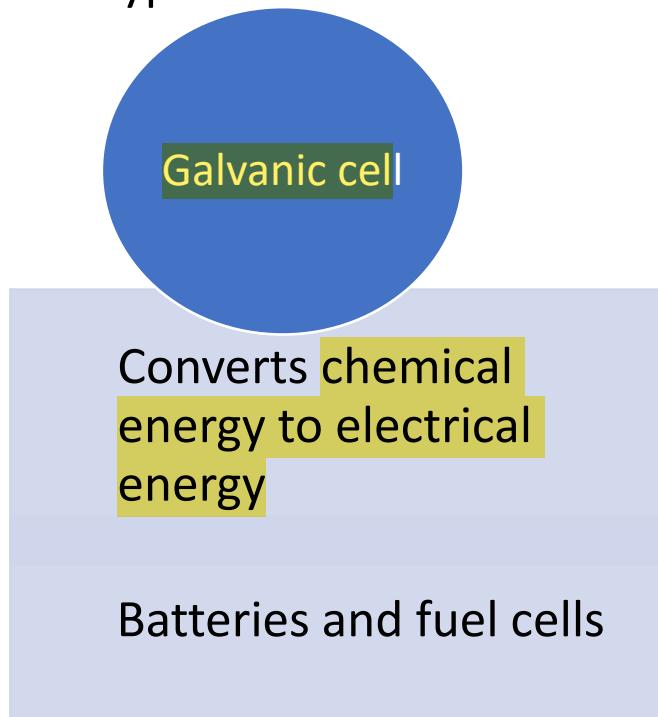
Module 1- Electrochemical equilibria

Electrochemistry

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



- Two types of cells:



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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

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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)

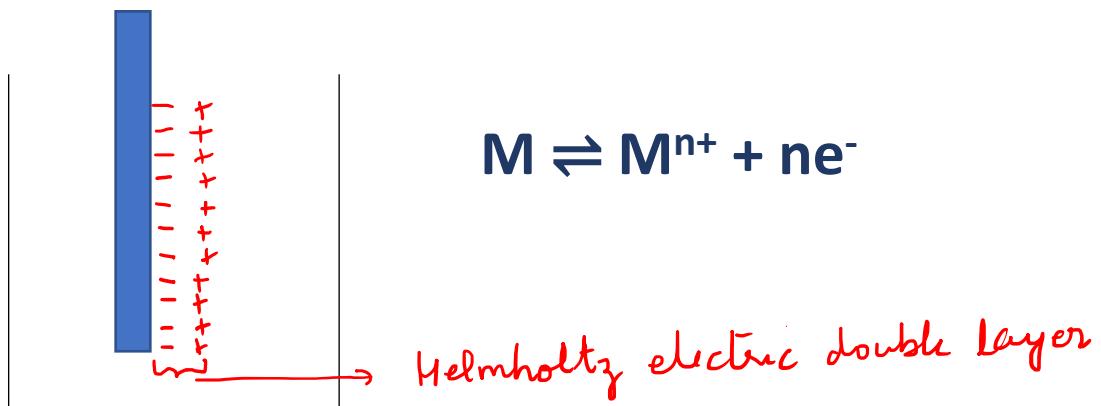


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Module 1- Electrochemical equilibria

➤ 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**

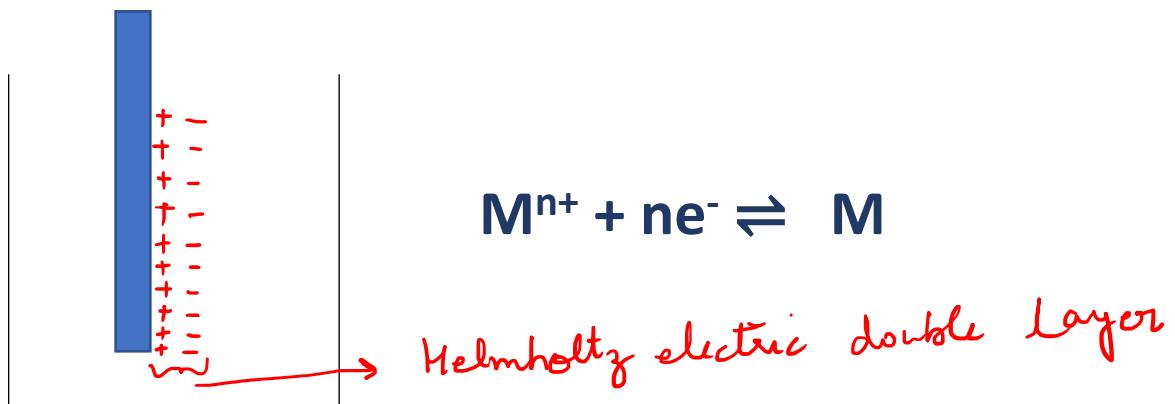


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Module 1- Electrochemical equilibria

➤ 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**



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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°

Electrochemical Cell

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

Cell notation

e.g. Daniel cell:



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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°_{cell}

Calculation of E_{cell}

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

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

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

- If reaction is spontaneous ΔG is negative, thus E_{CELL} should be positive
- If reaction is non spontaneous ΔG is positive, thus E_{CELL} should be negative

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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


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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

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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 ΔG , ΔG° and Q , we get

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

Where, E° = 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 C mol^{-1}

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

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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⁻s transferred, E°_{cell} = std. emf of the cell



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Lata Pasupulety

Department of Science and Humanities

latapasupulety@pes.edu

+91 80 6666 3333 Extn 759



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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*

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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

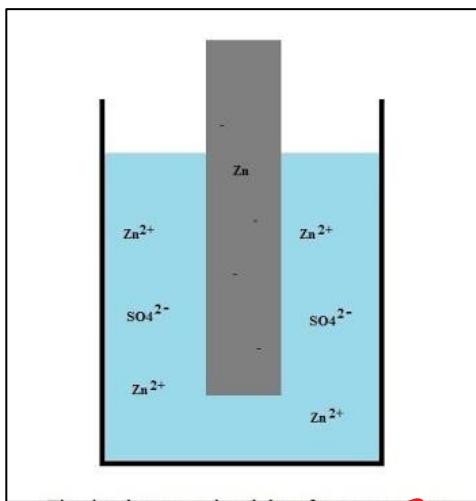
1. Metal-metal ion electrode:

- Metal in contact with a solution of its own ions

e.g., Zn/Zn²⁺, Cu/Cu²⁺, Ag/Ag⁺

- $M^{n+} + ne^- \rightleftharpoons M$
- 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)

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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

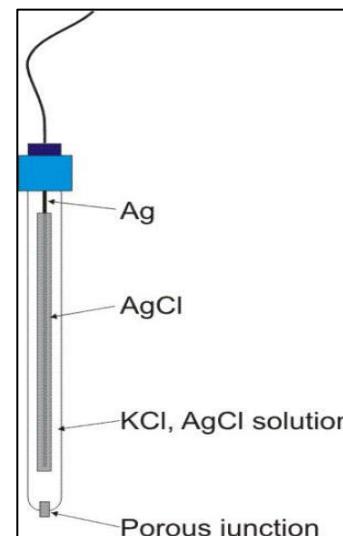
e.g., Calomel electrode $\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{KCl}$, $\text{Ag}/\text{AgCl}(\text{s})/\text{HCl}$

- 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>

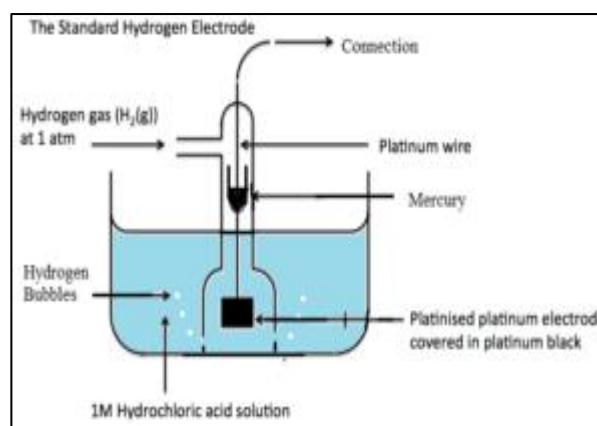
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3. Gas electrode:

- 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/H₂/H⁺, Chlorine electrode Pt/Cl₂/Cl⁻
- 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/

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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

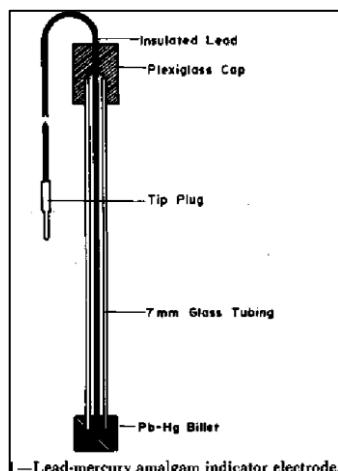
e.g., Lead amalgam electrode Pb-Hg/Pb²⁺

- 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>

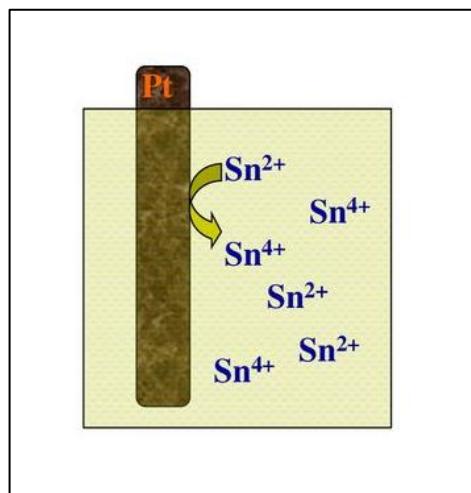
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Module 1- Electrochemical equilibria

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/Fe²⁺,Fe³⁺, Pt/Ce³⁺,Ce⁴⁺, Pt/Sn²⁺,Sn⁴⁺
- For stannous stannic electrode
 $\text{Sn}^{4+} + 2\text{e}^- \rightleftharpoons \text{Sn}^{2+}$
- Nernst equation:

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



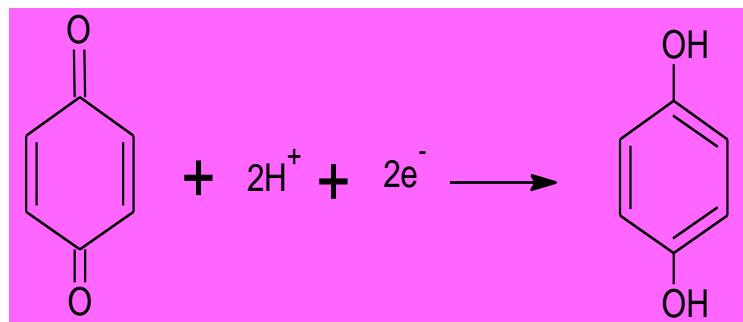
Source:<https://slideplayer.com/slide/13860805/>

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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,QH₂



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

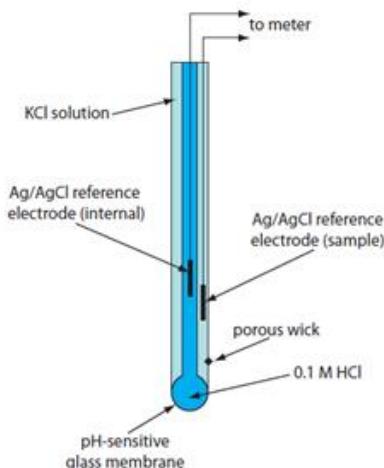
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Module 1- Electrochemical equilibria

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 H^+ , Na^+ , 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/



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Lata Pasupulety

Department of Science and Humanities

latapasupulety@pes.edu

+91 80 6666 3333 Extn 759



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Lata Pasupulety

Department of Science and Humanities

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Module 4- Electrochemical equilibria



Class content:

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

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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

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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

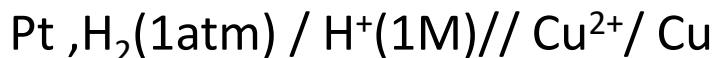
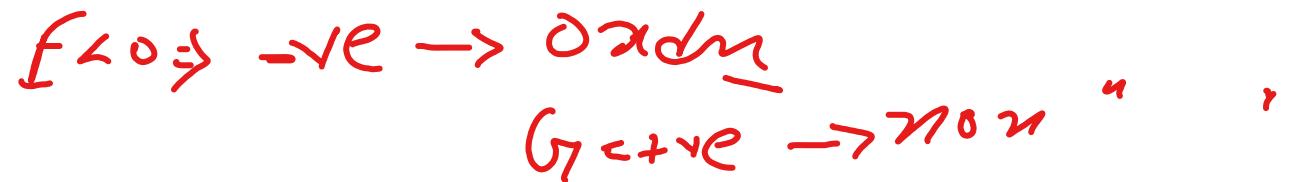
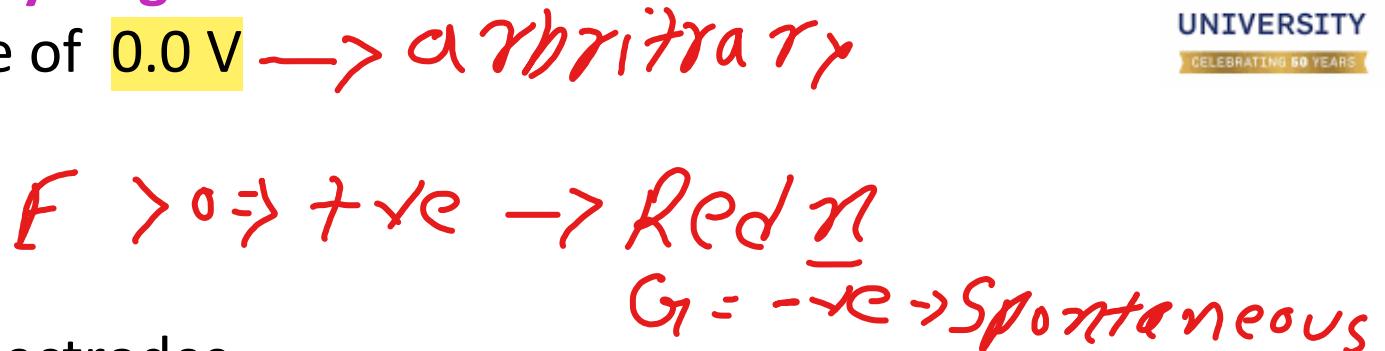
e.g.,



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

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

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



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

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

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

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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**

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Module 1- Electrochemical equilibria

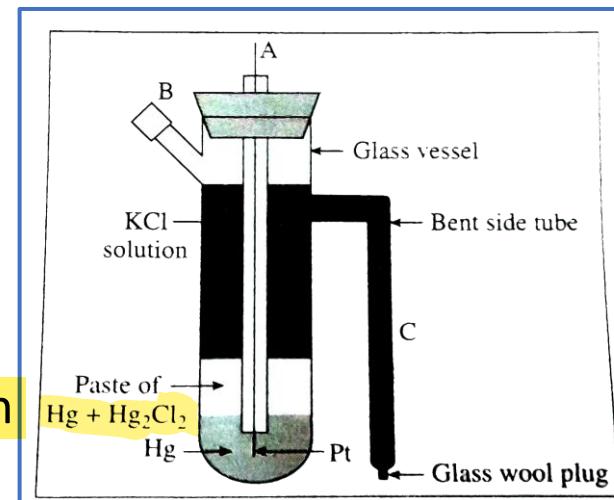
Secondary Reference electrodes:

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 Hg_2Cl_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>

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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:



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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



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Department of Science and Humanities

latapasupulety@pes.edu

+91 80 6666 3333 Extn 759



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Module 1- Electrochemical equilibria



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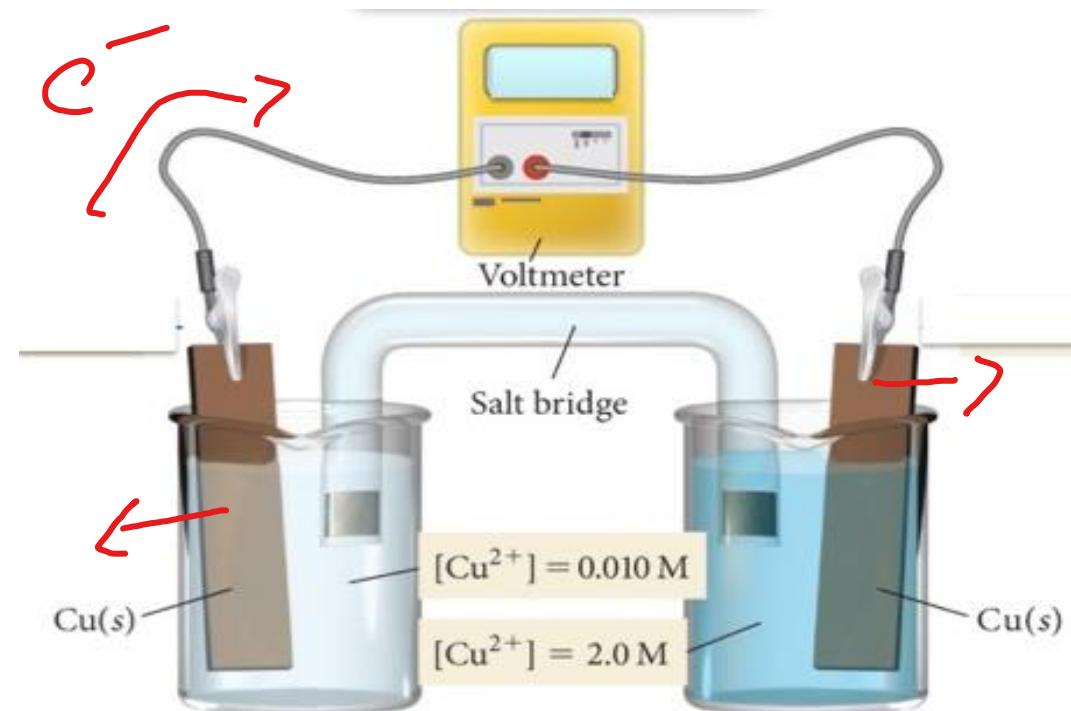
- ***Concentration cells***
 - *Types of concentration cells*
 - *Electrolyte concentration cells*
 - *Electrode concentration cells*
- ***Ion-selective electrodes***
 - *Types of ion – selective electrodes*
 - *Electrode potential for an ion-selective electrode*

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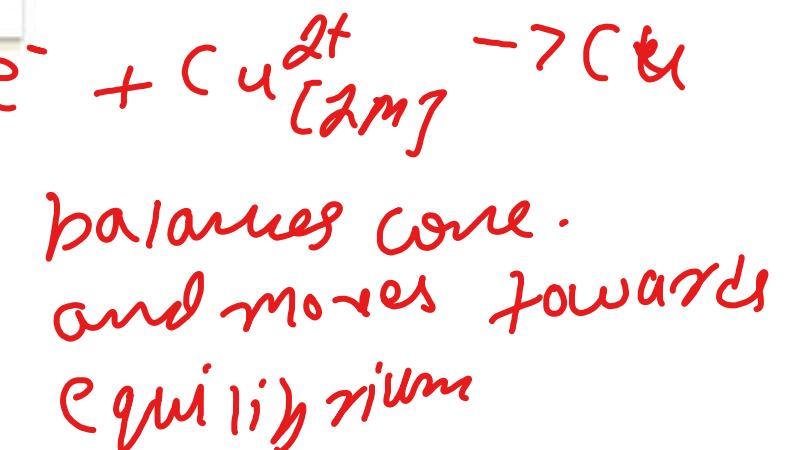
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Concentration cells:

- 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-



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Module 1- Electrochemical equilibria

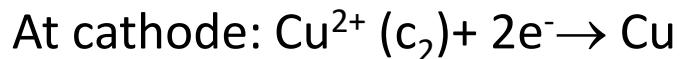
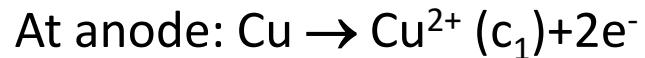
- In this cell 2 copper electrodes are immersed in copper sulphate solutions of concentration c_1 & c_2 , such that $c_2 > c_1$
- An electrolyte has spontaneous tendency to diffuse from a solution of higher concentration to a solution of lower concentration which is the **driving force** for development 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.

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Module 1- Electrochemical equilibria

Reactions :



Expression for cell potential:

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

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

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

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

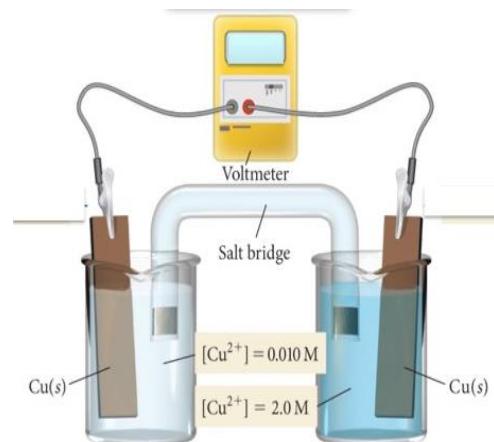
$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \left(\frac{c_2}{c_1} \right)$$

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

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- 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



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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

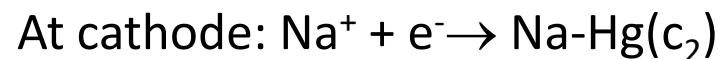
$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{\text{Na-Hg}(c_1)}{\text{Na-Hg}(c_2)}$$

ENGINEERING CHEMISTRY

Module 1- Electrochemical equilibria

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

Reactions are :



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

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

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

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

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Module 1- Electrochemical equilibria



- Pt/H₂(p₁ atm)/H⁺/H₂(p₂ atm)/Pt :

Nernst Equation:

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

- Pt/Cl₂(p₁ atm)/Cl⁻/Cl₂(p₂ atm)/Pt :

Nernst Equation:

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

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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 LaF_3 selective to F^-

Polycrystalline such as Ag_2S selective to S^{2-}

- **Non-crystalline membrane electrodes:**

e.g., Glass membrane selective to H^+ , Na^+

- **Liquid membrane electrodes:**

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

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

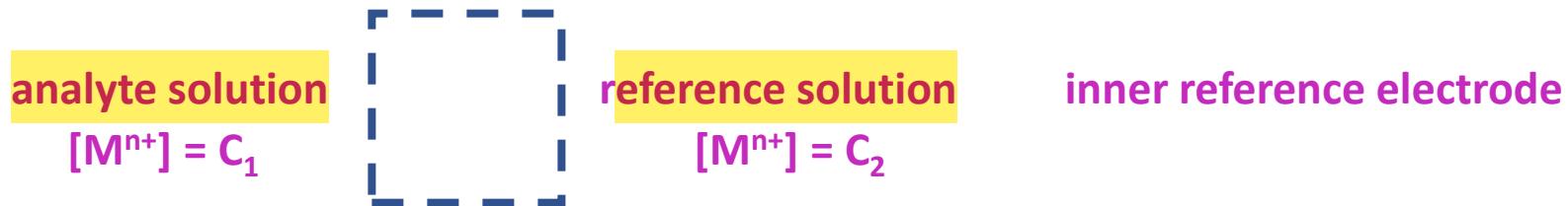
e.g., immobilized ion exchanger in PVC matrix ; used for Ca^+ , NO_3^-

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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

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

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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

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

E_{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

+91 80 6666 3333 Extn 759



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Module 1- Electrochemical equilibria



Class content:

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

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Module 1- Electrochemical equilibria



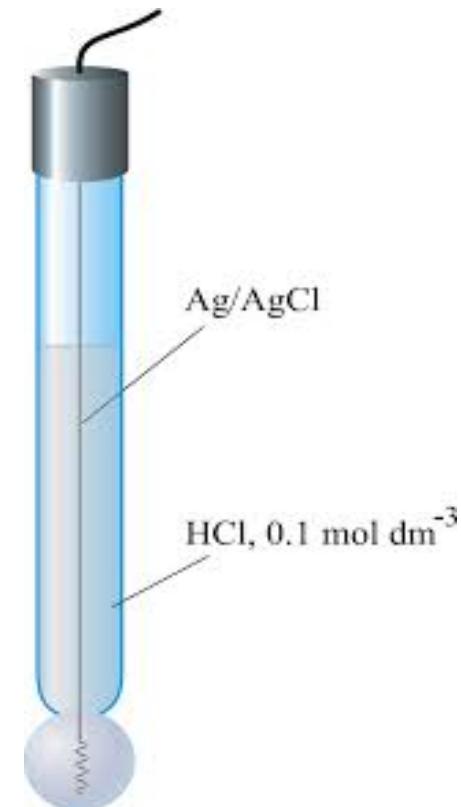
Glass electrode

- 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 H^+ ions

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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>

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Module 1- Electrochemical equilibria

Working:

analyte solution



reference solution

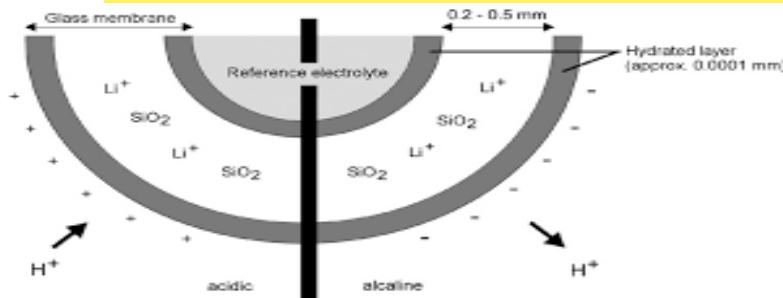
Ag-AgCl electrode

$$[H^+] = C_1$$

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



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



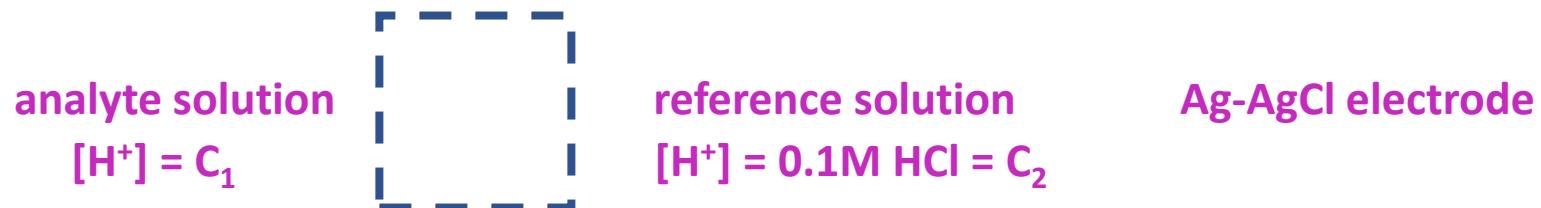
Source:http://www.metrohmsiam.com/teachingresearch/TRL 25/TRL25_955207_80155013.pdf

- 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

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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^+ , $n = 1$

$$E_b = L' - 0.0591pH$$

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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

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

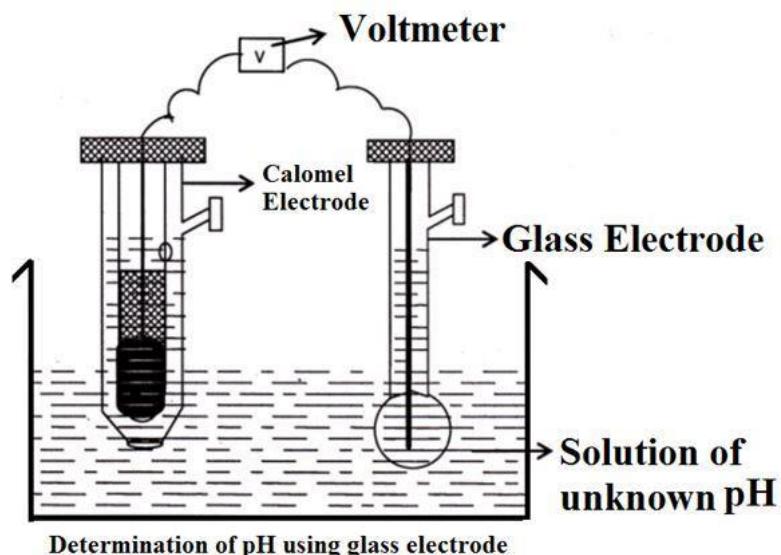
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Module 1- Electrochemical equilibria

Determination of pH using glass electrode:

- Glass electrode is combined with an external reference electrode

Hg/Hg₂Cl₂/Cl⁻//analyte solution/glass/0.1N HCl/AgCl/Ag



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

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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

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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

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Module 1- Electrochemical equilibria

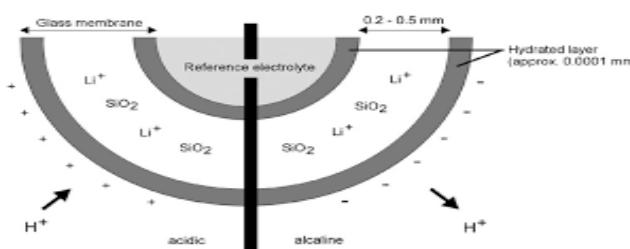
Disadvantages of glass electrode:

- 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 H^+ ions in the gel layer around the sensitive electrode membrane are replaced by Na^+ ions

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





THANK YOU

Lata Pasupulety

Department of Science and Humanities

latapasupulety@pes.edu

+91 80 6666 3333 Extn 759



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Module 1 – Electrochemical Equilibria



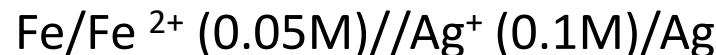
Class content:

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

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Module 1 – Electrochemical Equilibria

1. For the given cell:



- (i) Write the overall cell reaction
(ii) Calculate E_{cell}° and E_{cell} at 25°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 : $\text{Fe} + 2\text{Ag}^+ \rightarrow \text{Fe}^{2+} + 2\text{Ag}$

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

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

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

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

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Module 1 – Electrochemical Equilibria



2. For the following concentration cell:



Calculate potential of the cell at 25°C.

Sol.

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

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

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

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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 Cl^- ion in the saturated calomel electrode, if the cell potential measured is 0.0988 V at 25°C.

Sol.



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

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

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

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

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

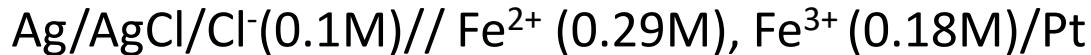
$$x = 4.69\text{M}$$

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Module 1 – Electrochemical Equilibria



4. For the following cell:

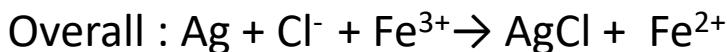
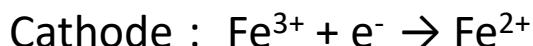


(i) Write the half cell reactions and overall cell reaction.

(ii) Calculate E_{Cell}° and E_{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: $\text{Ag} + \text{Cl}^- \rightarrow \text{AgCl} + \text{e}^-$



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

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

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

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

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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.

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

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

$$n = 3 ,$$

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

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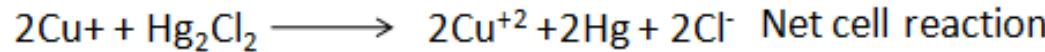
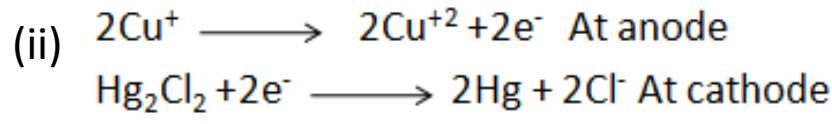
Module 1 – Electrochemical Equilibria

6. A decinormal calomel electrode is used to determine the potential of the following redox electrode : Pt/Cu²⁺(0.58 M),Cu⁺(0.08M)

- (i) Write cell representation.
- (ii) Write the reactions at the electrodes
- (iii) Calculate E⁰_{cell} and E_{cell} at 298 K.

(Given : E⁰_{Hg/Hg₂Cl₂/Cl⁻} = 0.281V , E_{Cu²⁺/Cu⁺} = 0.153 V)

Sol. (i) Pt/Cu²⁺(0.58 M),Cu⁺(0.08M)//Cl⁻(0.1 M)/Hg₂Cl₂/Hg



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

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

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

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

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Module 1 – Electrochemical Equilibria



7. For the following cell:



- Write the half cell reactions.
- Calculate E_{cell}° and E_{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) $E_{\text{cell}}^{\circ} = E_{\text{C}}^{\circ} - E_{\text{A}}^{\circ} = 1.52 + 0.44 = 1.96 \text{ V}$

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

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

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

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

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

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

$$\text{pH} = 4.12$$



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Lata Pasupulety

Department of Science and Humanities

latapasupulety@pes.edu

+91 80 6666 3333 Extn 759



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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*

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Module 2- Corrosion Chemistry



Class content:

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

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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**

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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



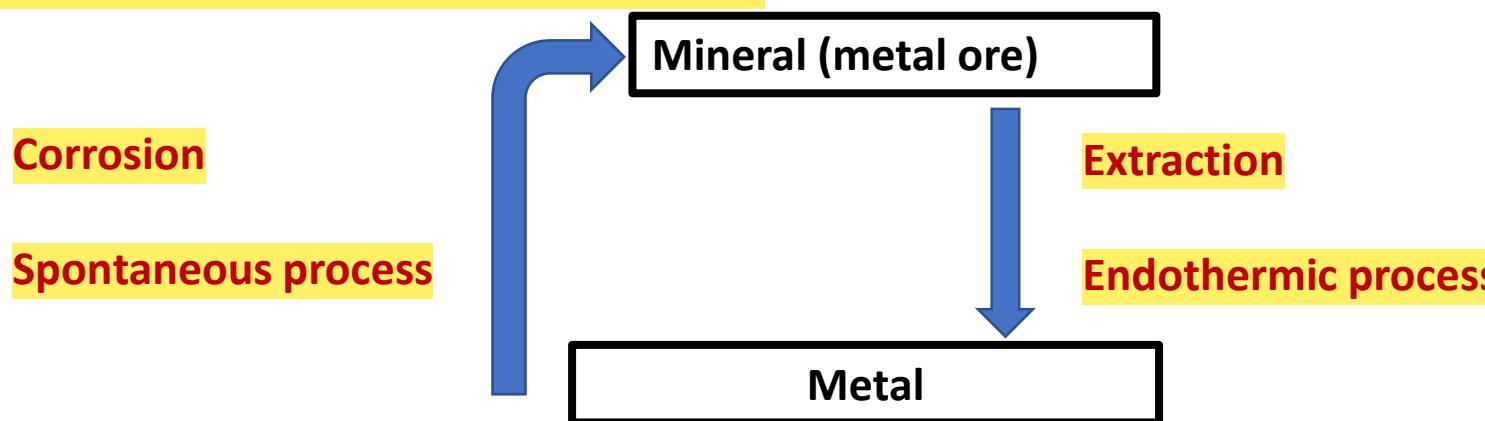
Exposure to the elements has resulted in the formation of the blue-green **patina** seen today

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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



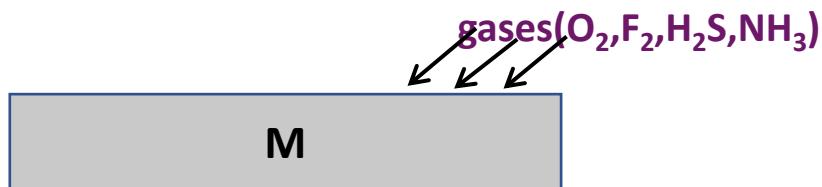
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Module 2- Corrosion Chemistry

Types of corrosion

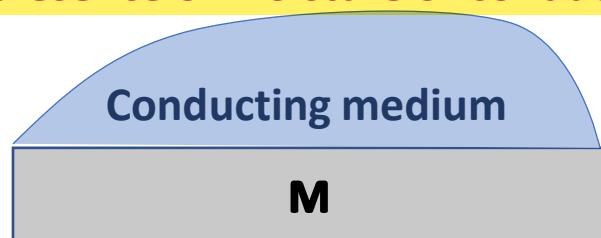
- **Dry corrosion :**

- 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



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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

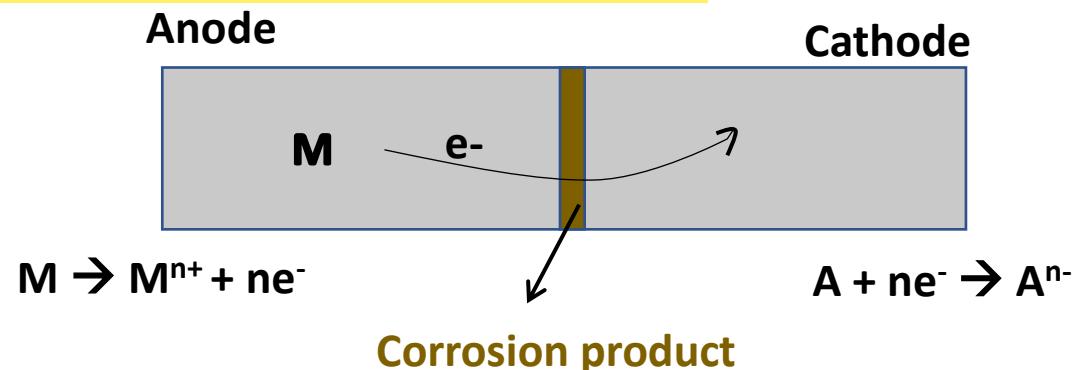
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Module 2- Corrosion Chemistry

- 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**



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Module 2- Corrosion Chemistry

Reactions:

- Anode:



e.g., when iron undergoes corrosion,



- Cathode:

- Liberation of hydrogen
- Absorption of oxygen

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Module 2- Corrosion Chemistry

- Liberation of hydrogen

- In acidic medium



- In neutral or alkaline medium



- Absorption of oxygen

- In acidic medium



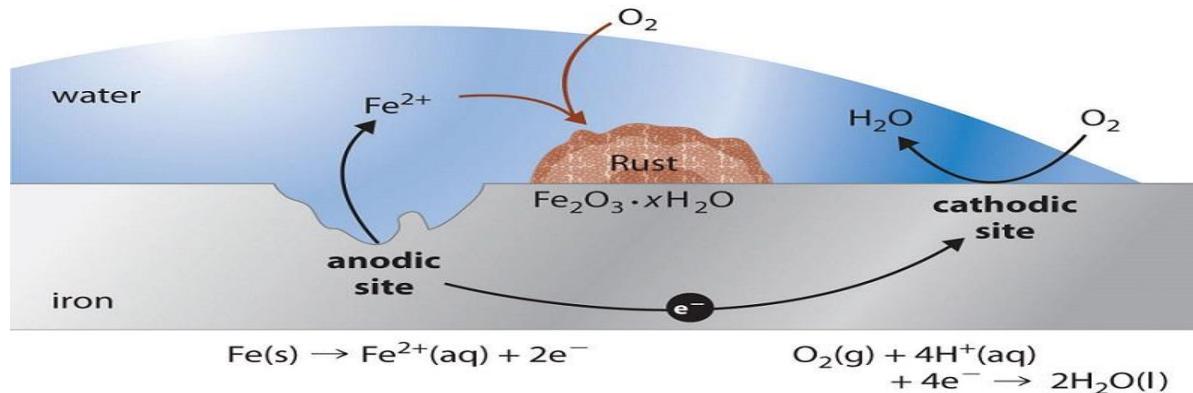
- In neutral or alkaline medium



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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)



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



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



- In the **presence of limited oxygen**, 4Fe(OH)_2 is converted into **magnetic oxide of iron (Fe_3O_4)** and is known as **black rust**





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Lata Pasupulety

Department of Science and Humanities

latapasupulety@pes.edu

+91 80 6666 3333 Extn 759



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Department of Science and Humanities

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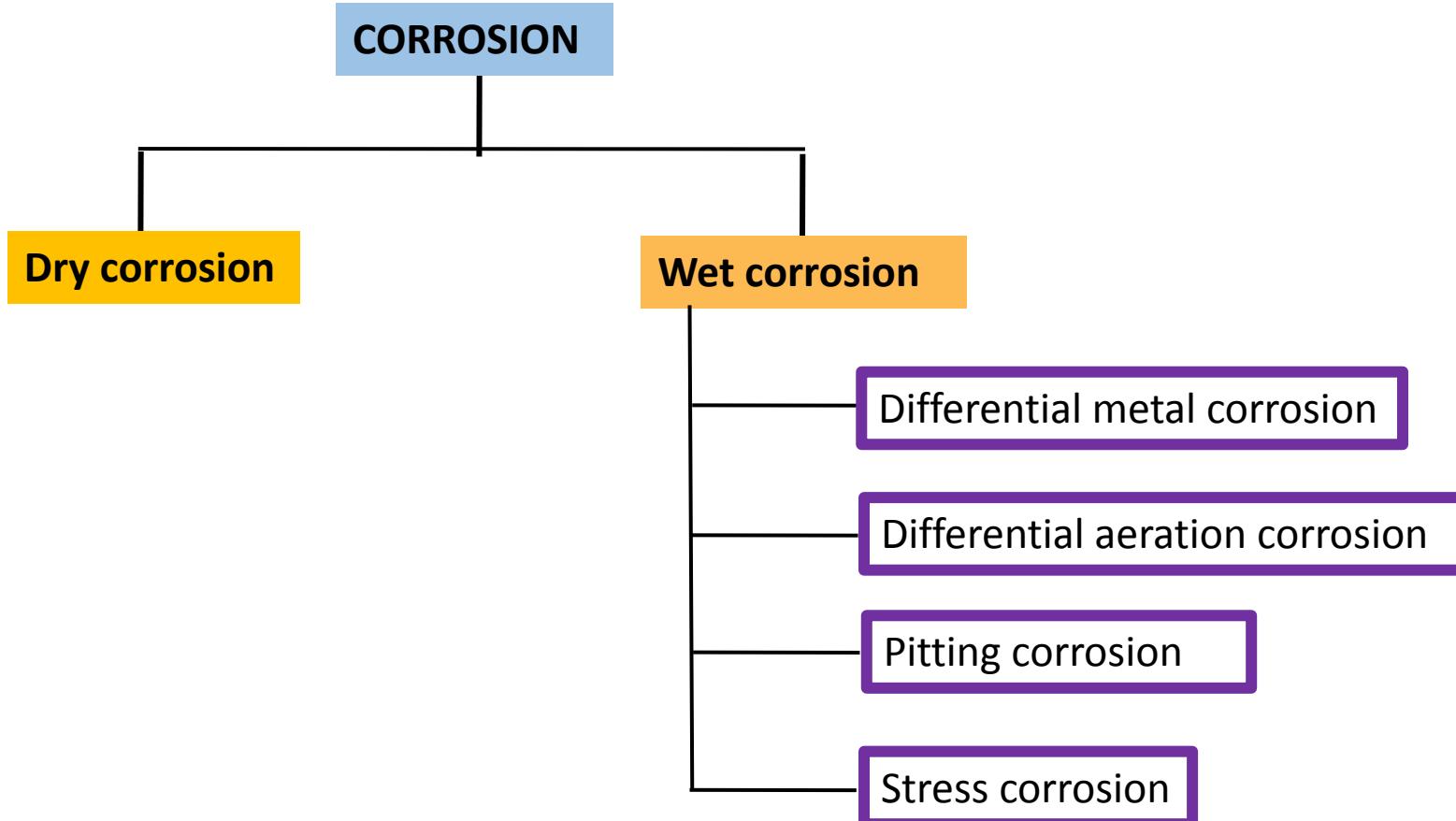
Class content:

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

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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

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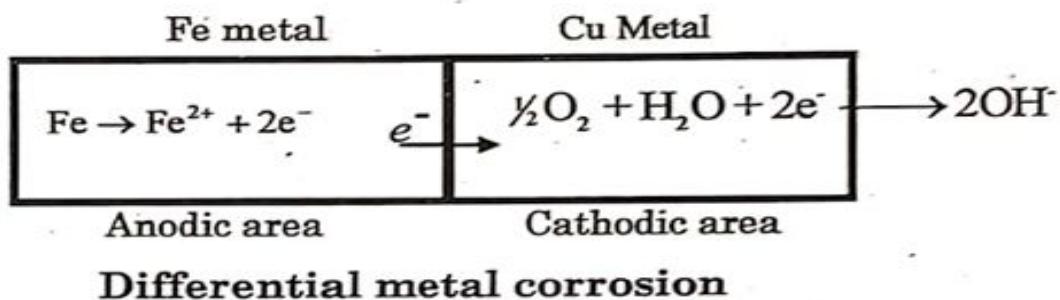
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Reactions:



Examples:

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

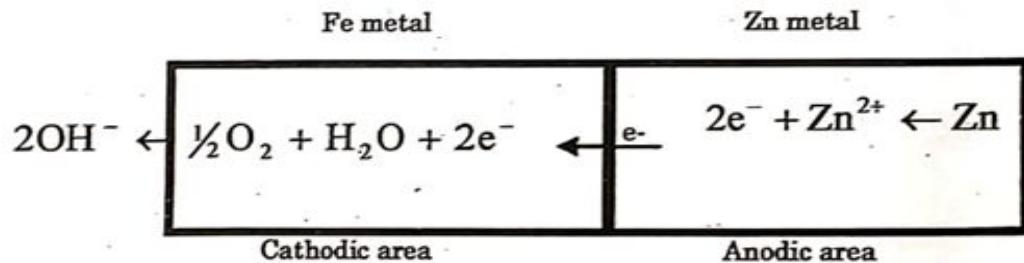


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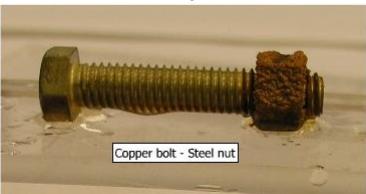
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- Iron in contact with zinc
 - Standard electrode potential of Zn (-0.76 V)
Fe (-0.44 V)



- 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-ide
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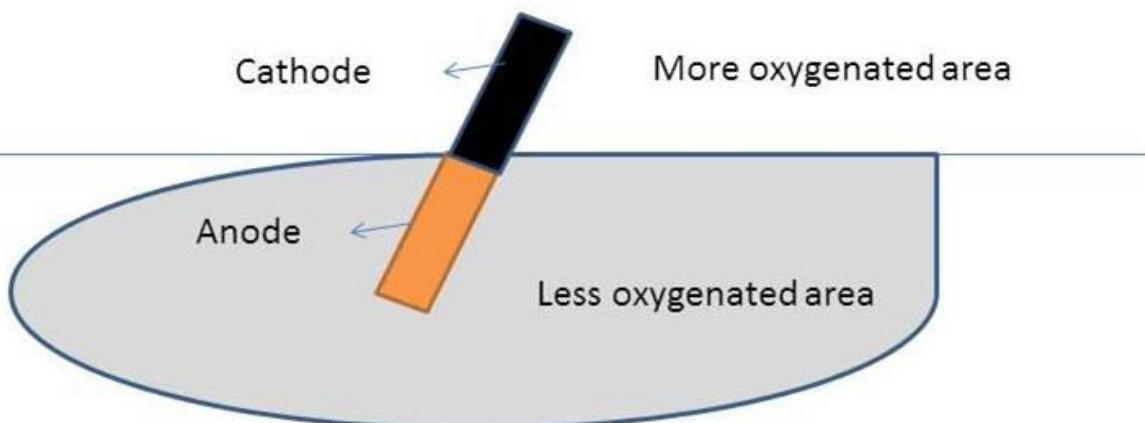
Differential aeration corrosion:

- 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

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Reactions:



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

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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

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Class content:

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

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Waterline corrosion:

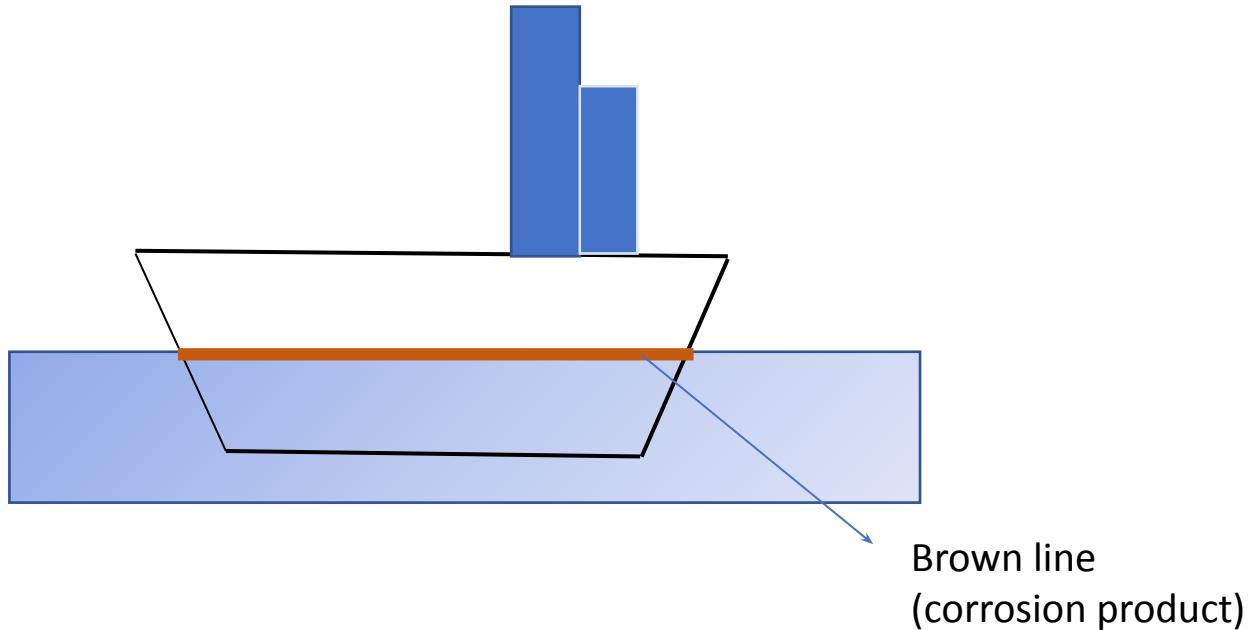
- A special case of **differential aeration corrosion**
- Observed when metal is **half immersed in water**
- The part **immersed in water** is exposed to less O_2 , hence acts as anode and **gets corroded** while the **part not in water** is exposed to more O_2 and acts as **cathode**; **remains unaffected**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

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Examples:

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

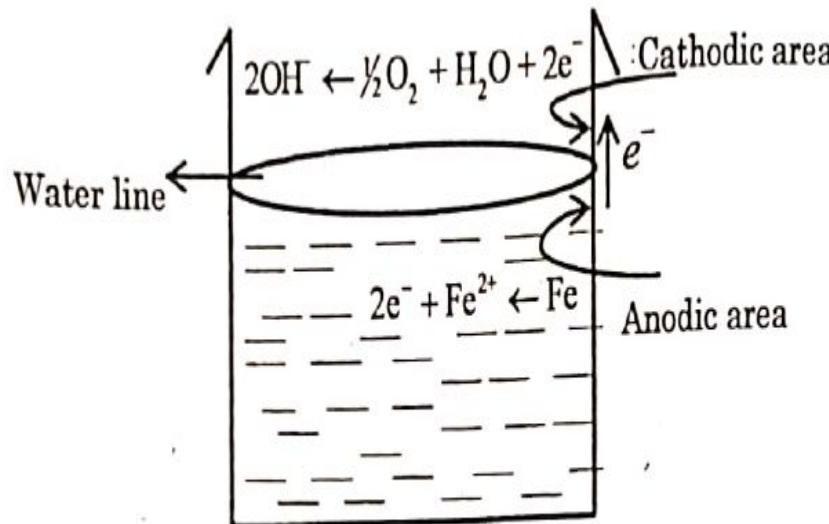


A **distinct brown line** is formed just below the water line due to the deposition of rust

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



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

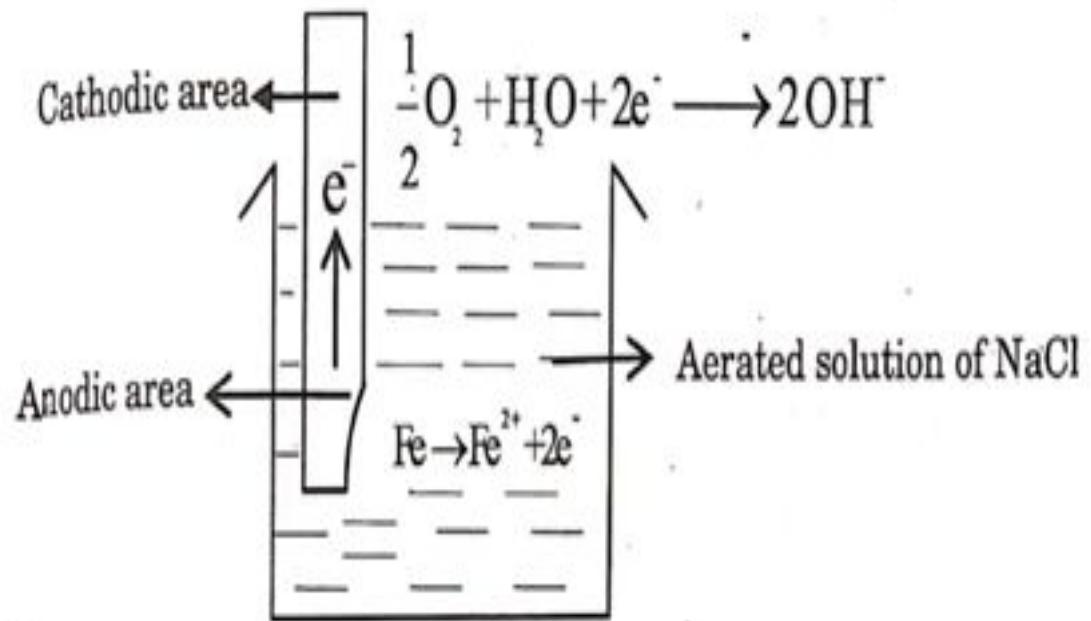
Water line corrosion

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

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- Iron rod partially dipped in NaCl solution



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

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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



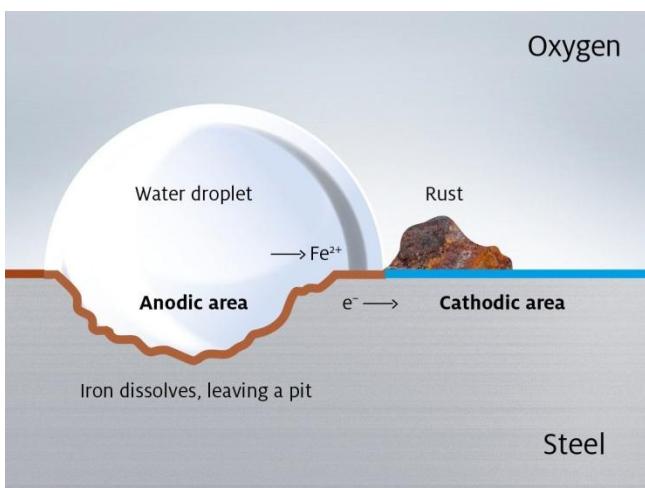
<https://www.nuflowmidwest.com/2-types-of-corrosion-that-occur-in-industrial-piping-systems/>

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- 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 O₂** becomes cathodic

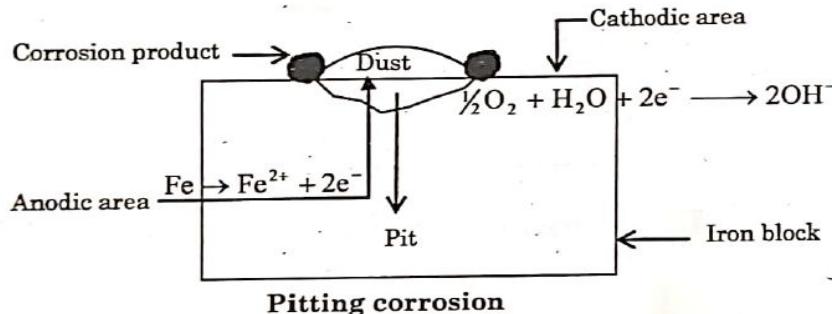


<https://www.bonderite.com/en/technologies/pretreatment/corrosion-protection.html>

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- 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:



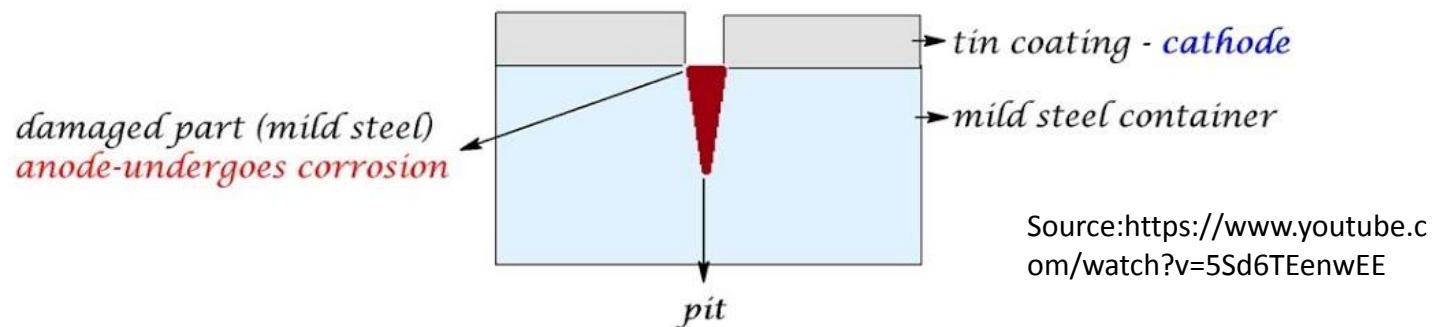
Source: Basuchandra's Engineering chemistry, Banbayalu (2014)

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- 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:





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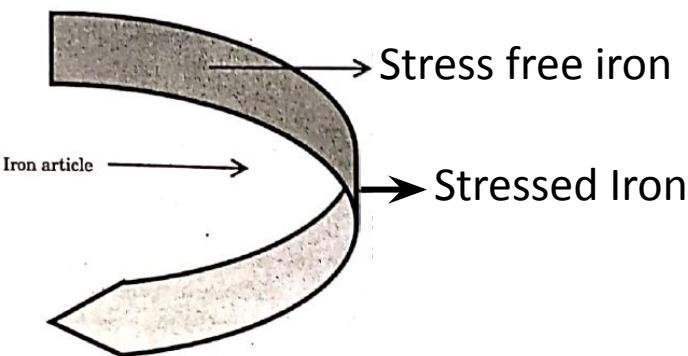


Class content:

- *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**

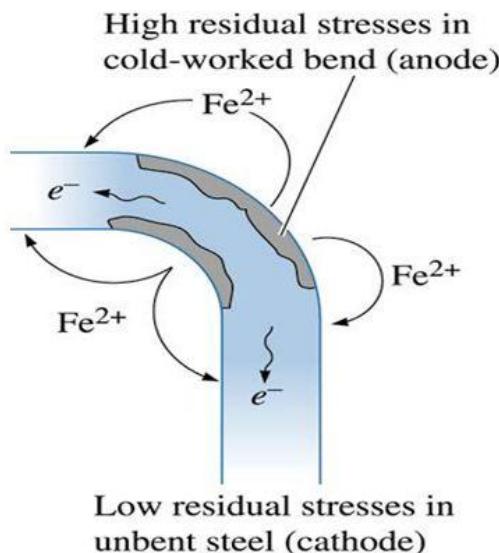


Source: Basuchandra's Engineering chemistry, Banbayalu (2014)

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- 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/>

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- 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

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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**

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- **Corrosion mechanism in water boilers:**

- When water is boiled, Na_2CO_3 present in boiler water is hydrolysed at high temperature to give NaOH
- 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, NaOH gets concentrated and when concentration of 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(Na_2FeO_2)undergoes further hydrolysis regenerating NaOH and Fe_3O_4 is produced which is brittle in nature
$$3\text{Na}_2\text{FeO}_2 + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2 + 6\text{NaOH}$$

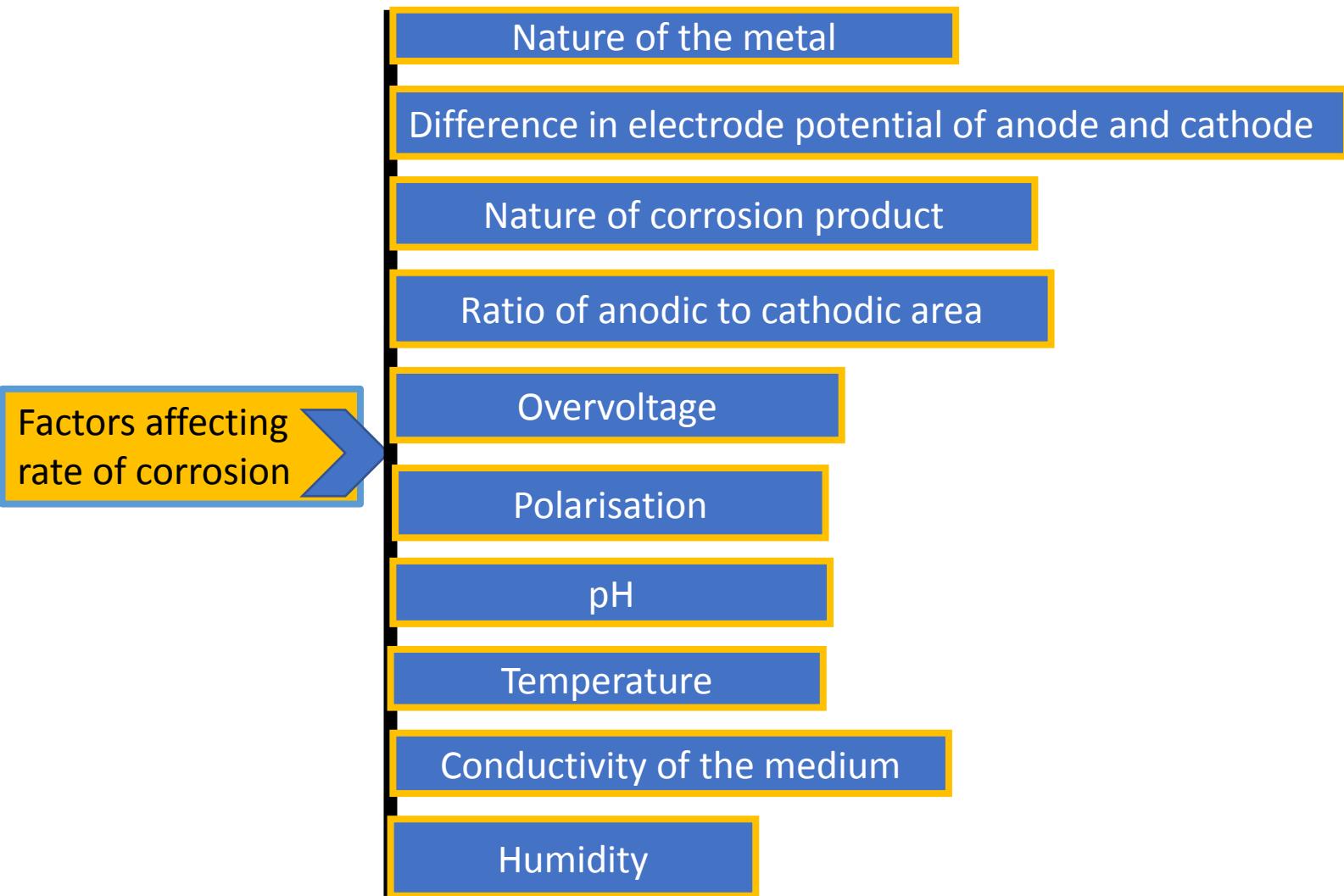
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- Cracks propagate along **intergranular path** which sometimes results in **explosion of the boiler**
- Since concentrated caustic soda is recognized as the specific environment required for stress corrosion of water boiler, this type of corrosion 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.**

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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

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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

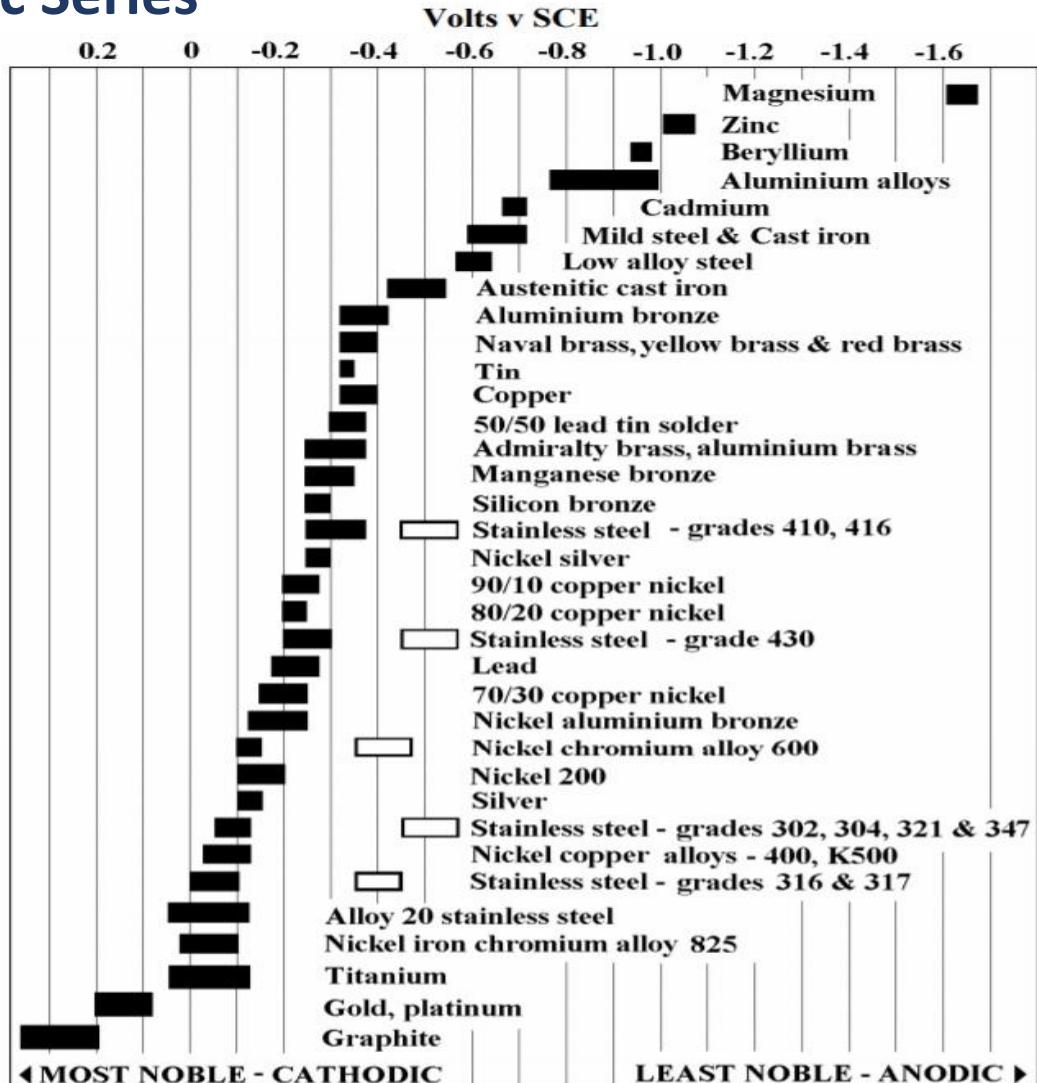
The electrochemical series is built up by arranging various redox equilibria in the order of their standard electrode potentials (redox potentials). The most negative E° values are placed at the top of the electrochemical series, and the most positive at the bottom

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

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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

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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

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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.

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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

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- 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



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Class content:

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

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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

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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)
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Metal Reducing Activity Increasing

Metal Oxidizing Activity Increasing

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

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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

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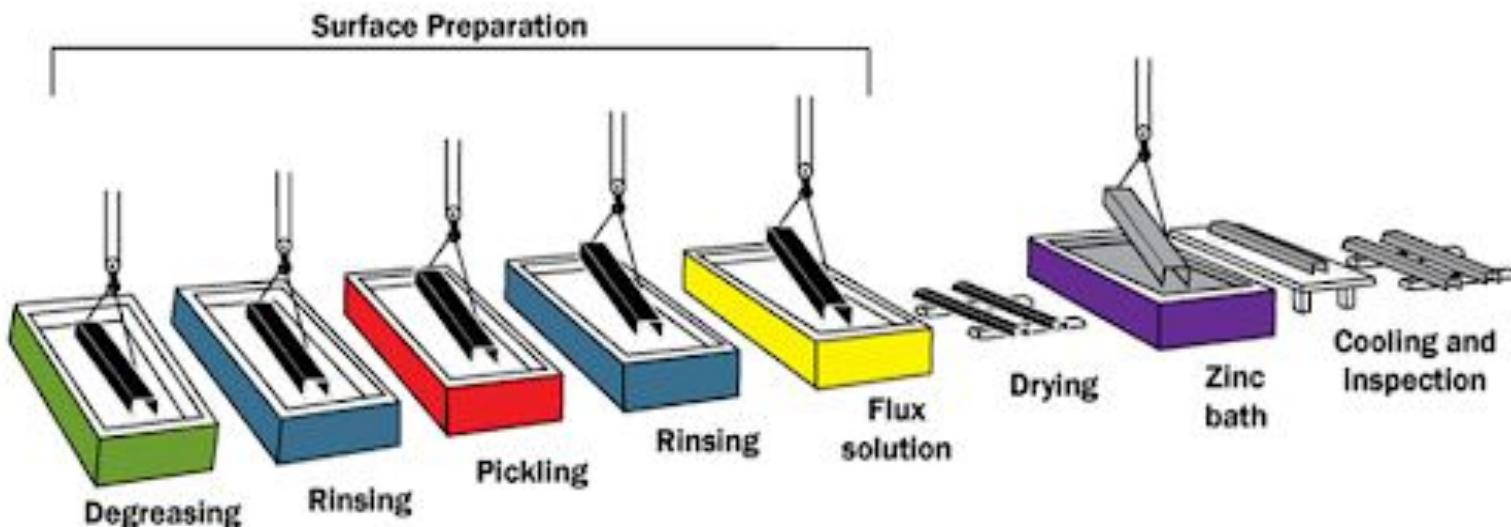
Galvanizing:

- 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

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Process of Galvanisation



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

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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:

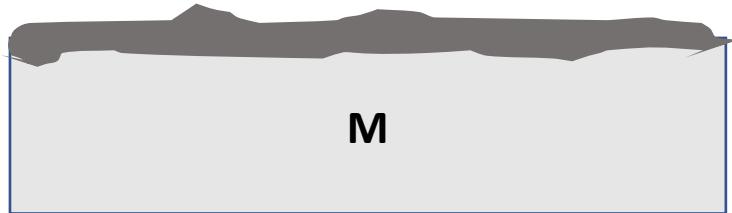
Galvanized articles are **not used for preparing and storing food** because **zinc dissolves in dilute acids** producing toxic zinc compounds

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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**

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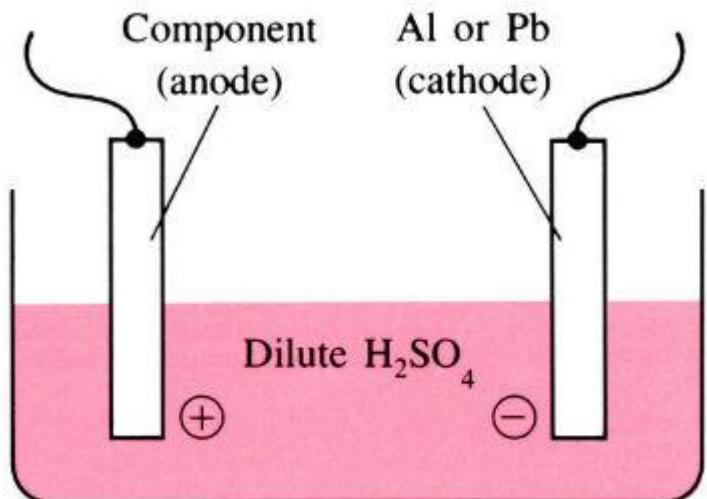
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Anodizing:

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>

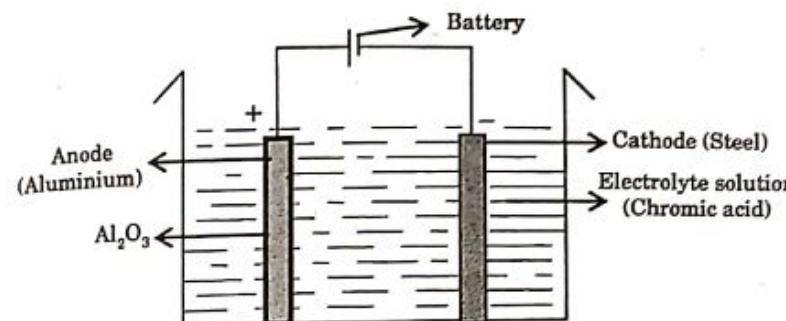
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Anodizing of Aluminum:

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°C
- Lead or steel is taken as **cathode**
- **Voltage** above 40V is applied
- Outer layer of **Al is oxidised to Al_2O_3**



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



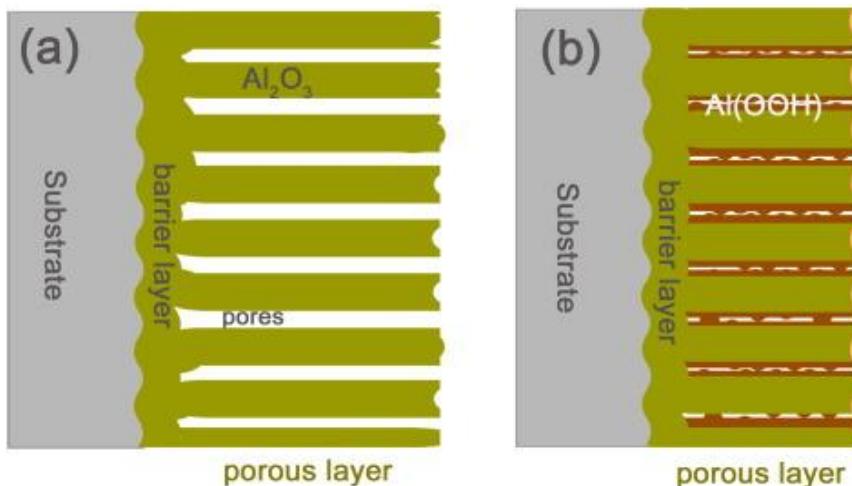
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Al_2O_3 formed on the surface is **slightly porous** in nature

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

Al_2O_3 is converted into $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ which occupies **higher volume**; the pores are sealed



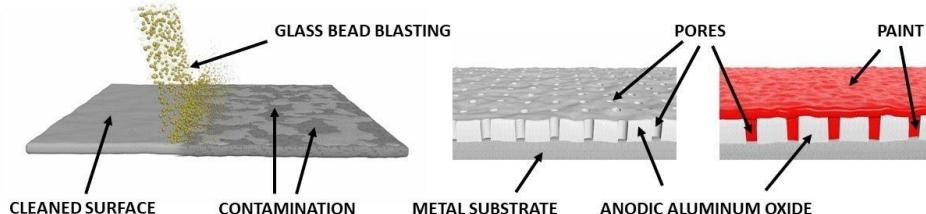
Source: <https://www.sciencedirect.com/science/article/abs/pii/S0257897215304540>

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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.

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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

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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



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- 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

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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

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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

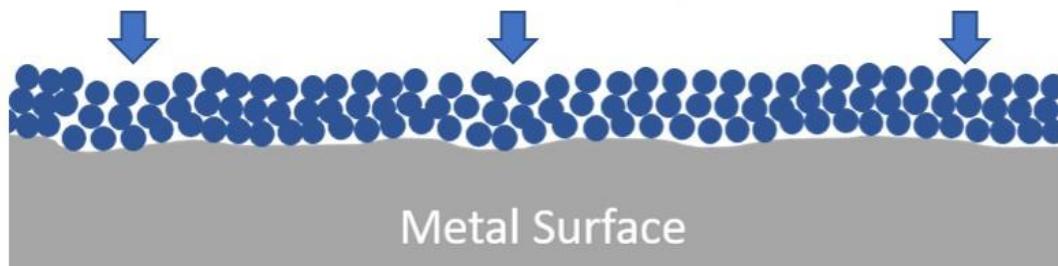
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Anodic inhibitors:



- 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(CrO_4^{2-}), tungstate (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>

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- 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 Na_2CrO_4 , Na_2WO_4**

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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

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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

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By increasing the hydrogen overvoltage on the metal surface –



- When Hydrogen overvoltage is high , **liberation of H₂** will be difficult
- By the addition of **oxides of arsenic, antimony**(As₂O₃, Sb₂O₃) or salts like **sodium meta-arsenite**(NaAsO₂)
 - They **deposit** on the cathode region
 - The **hydrogen overvoltage on these metals is very high**; liberation of H₂ is reduced

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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.



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By decreasing the diffusion rate of oxygen to cathode –

- By adding salts with large cations such as ZnSO_4 , MgSO_4 , NiSO_4 etc.
- The **cations** of the salts (Zn^{2+} , 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

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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

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Module 6- Corrosion Chemistry



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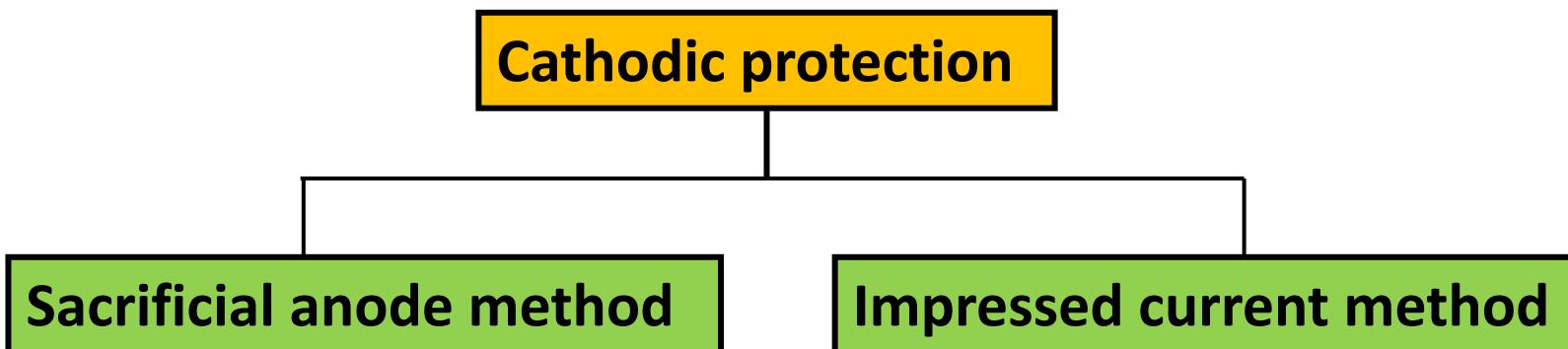
- *Corrosion control*
 - *Cathodic protection*
 - *Sacrificial anode method*
 - *Impressed cathodic current method*

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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



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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**

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Module 6- Corrosion Chemistry

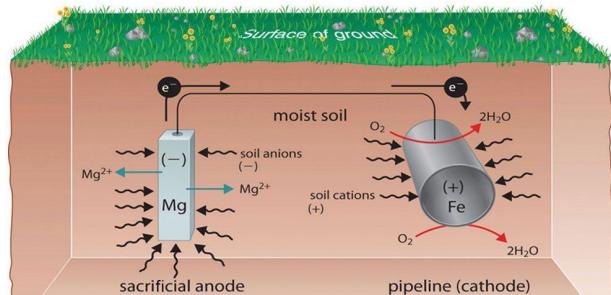
Examples:

- 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**

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Advantages:

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

Disadvantages:

- Involves recurring expenditure for replacement of consumed anodes

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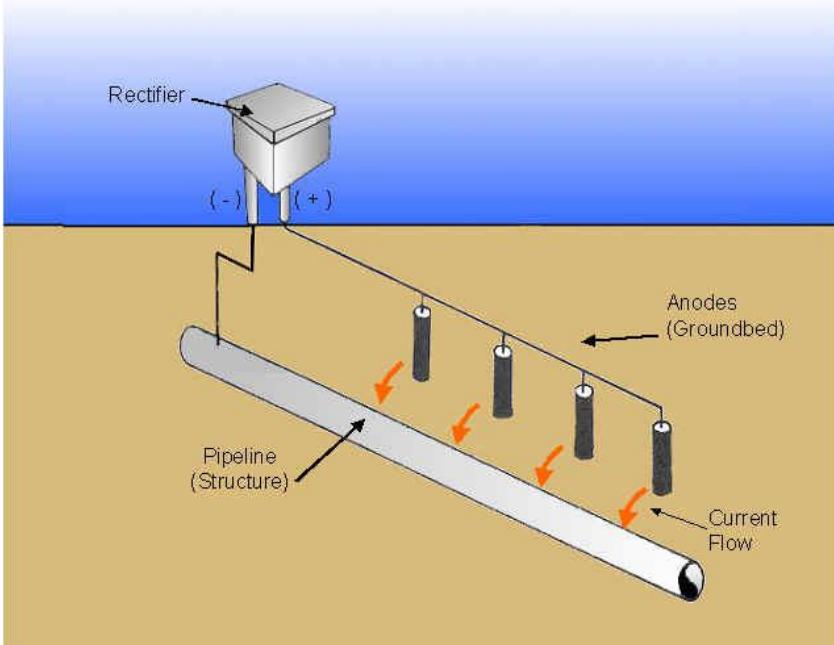
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Impressed current method:

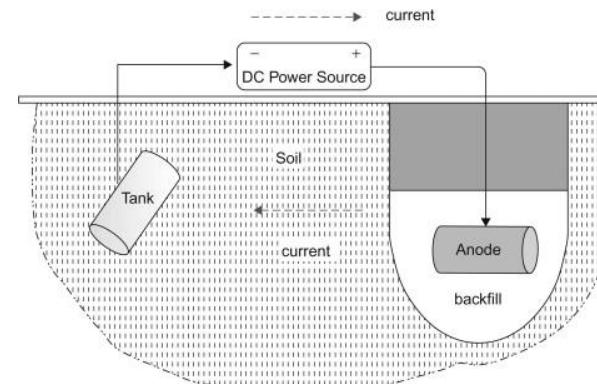
- By applying a **direct current**
- The **protected metal is made cathodic** by connecting it to the cathode of the external source of current
- Anode of the external source is usually connected to an **inert electrode** like graphite; Platinum, silicon, iron are also used as anodes
- A **backfill of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

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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>

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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

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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

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Module 6- Corrosion Chemistry



Class content:

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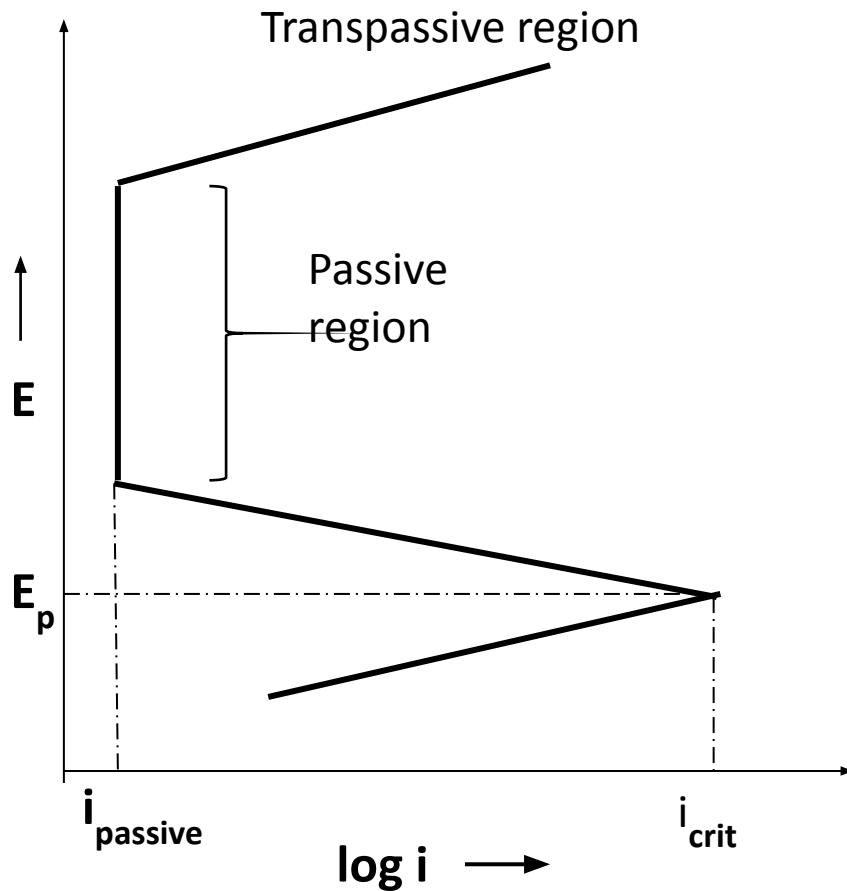
Anodic protection:

- 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

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Module 6- Corrosion Chemistry

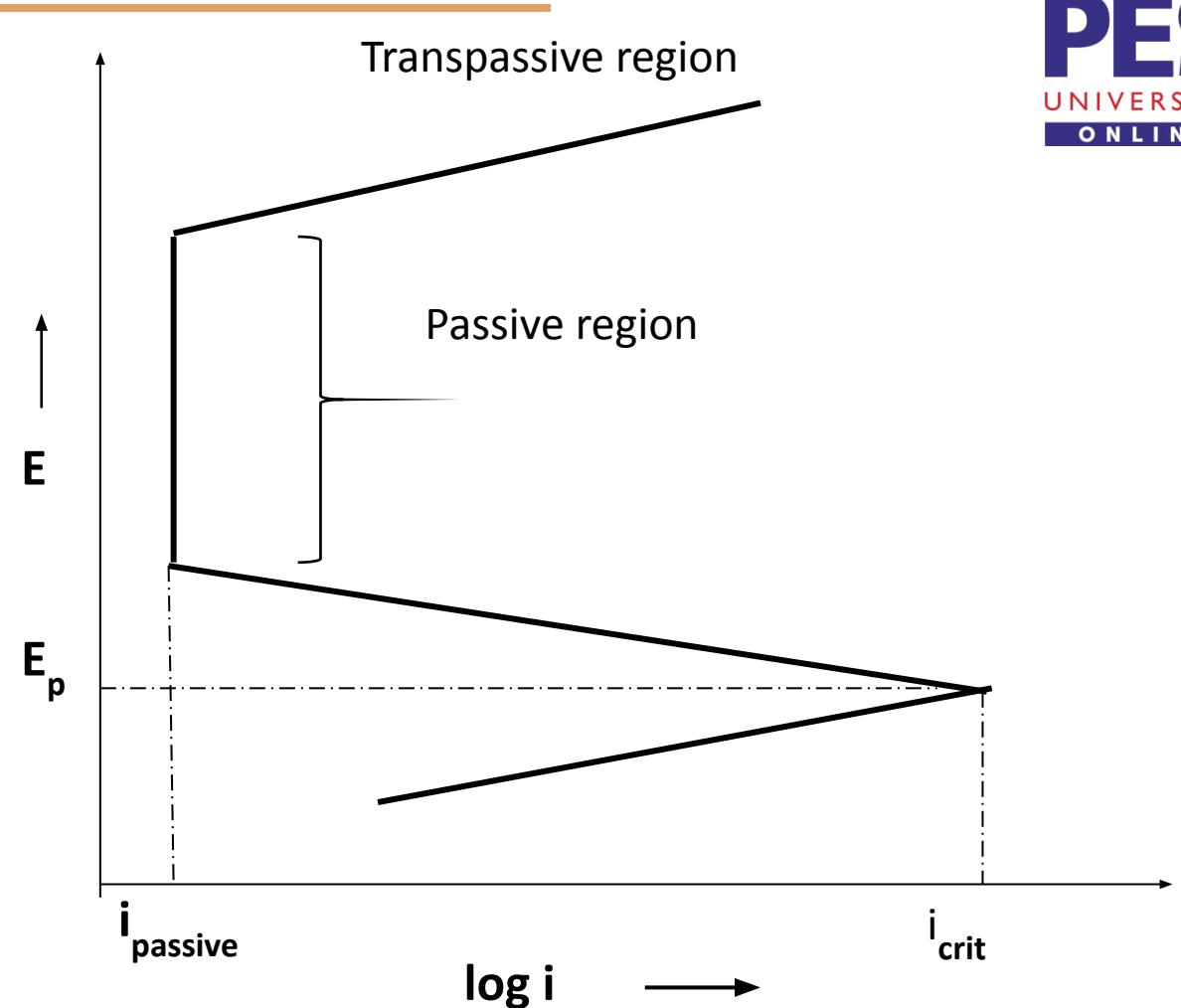
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Module 6- Corrosion Chemistry

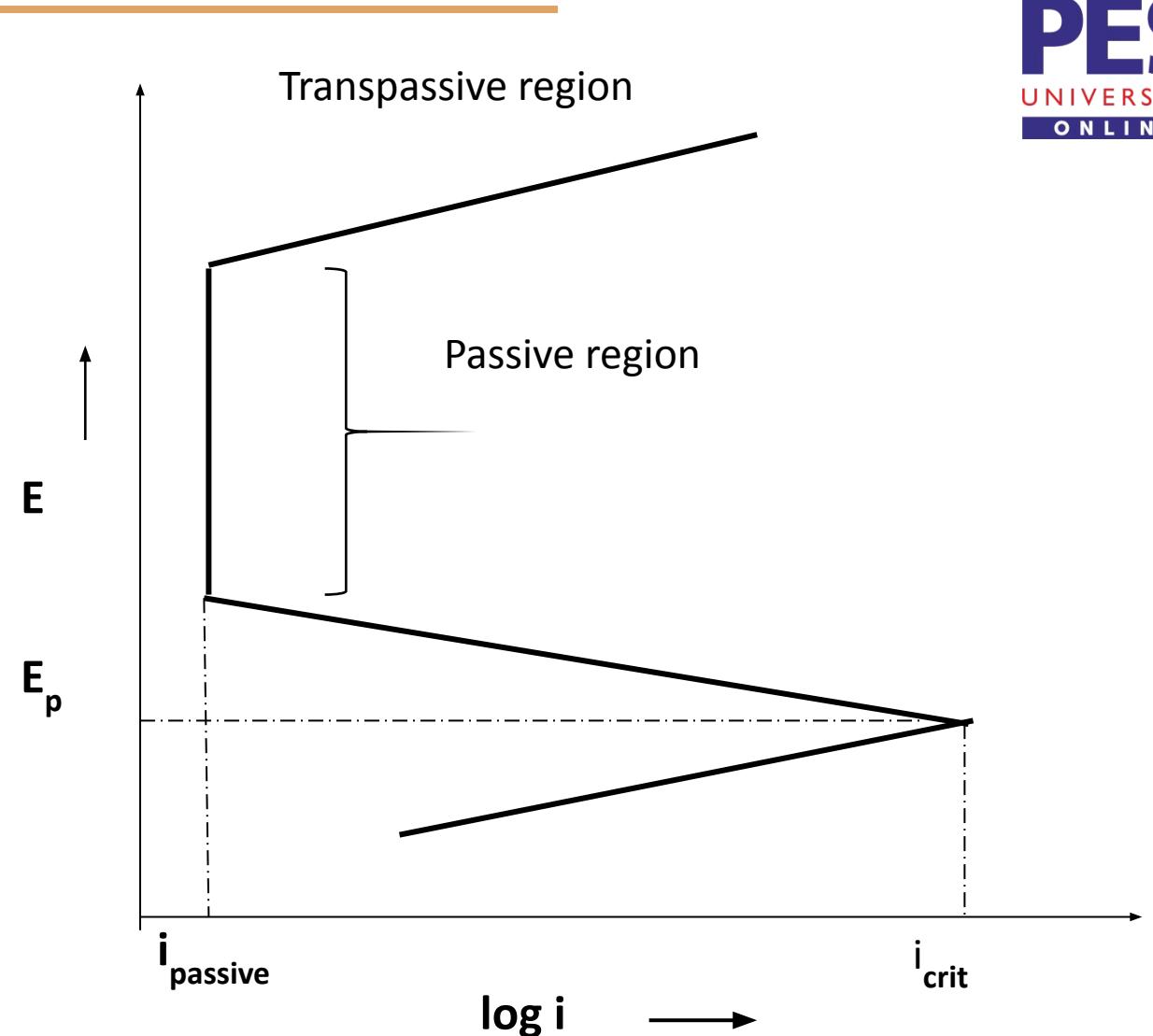
- A known **potential** is applied to the metal specimen and **current** is measured
- As the potential is increased, initially the **current also increases**, and it indicates the dissolution of metal
- This trend continues until the current reaches a **critical value (i_{crit})** and passivation due 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)**



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Module 6- Corrosion Chemistry

- Above E_p , the current flow decreases and reaches a minimum value called **passivation current, i_{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**
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Module 6- Corrosion Chemistry



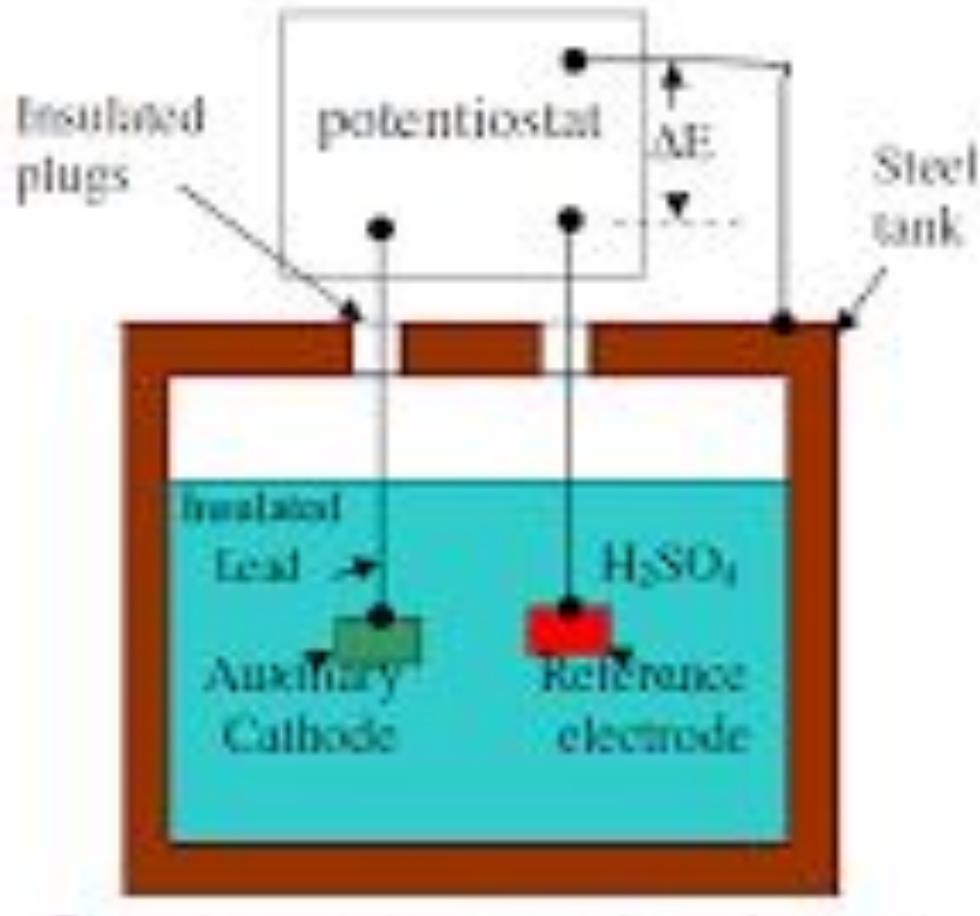
Anodic protection to a structure is applied by using a device called **potentiostat**

- 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

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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

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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



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Department of Science and Humanities



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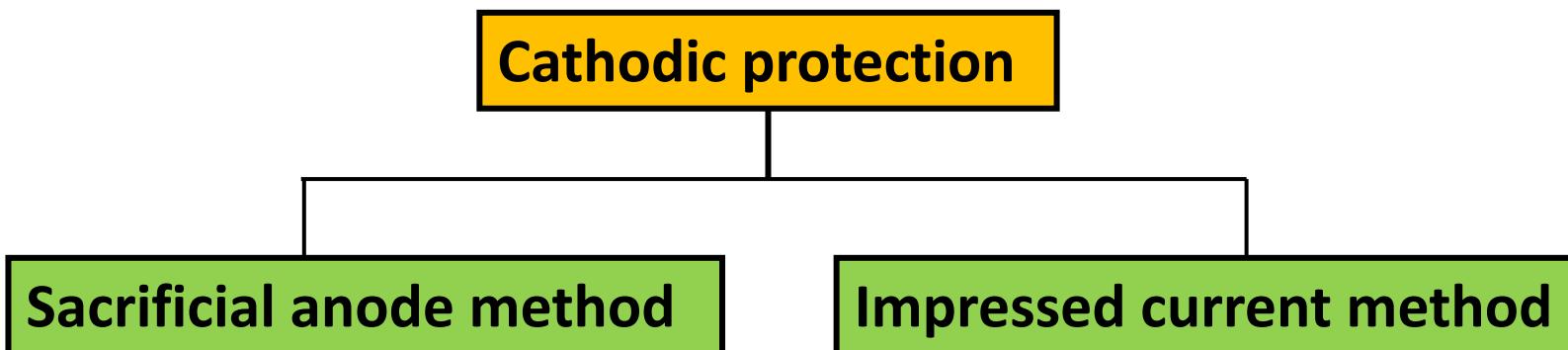
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Module 6- Corrosion Chemistry

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Module 6- Corrosion Chemistry

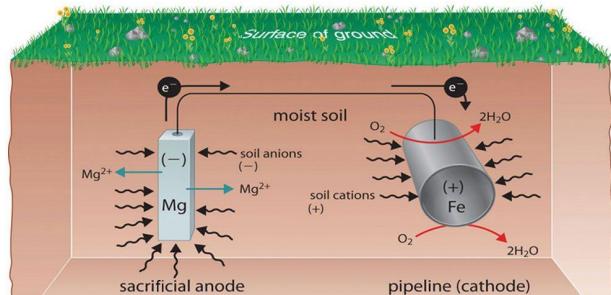
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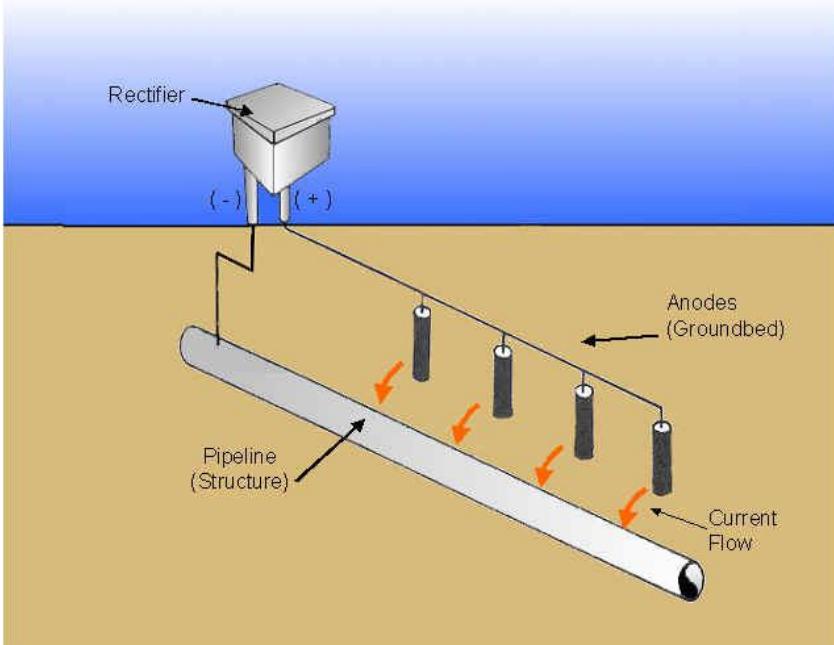
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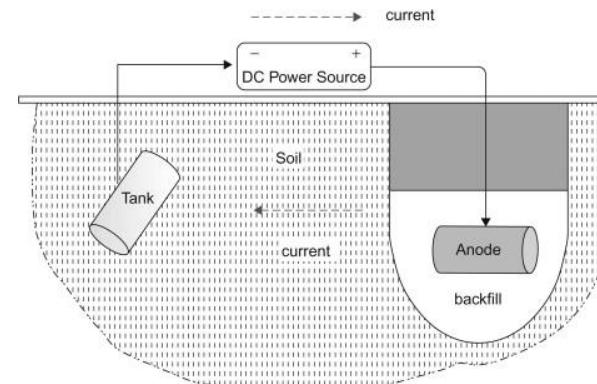
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Module 6- Corrosion Chemistry



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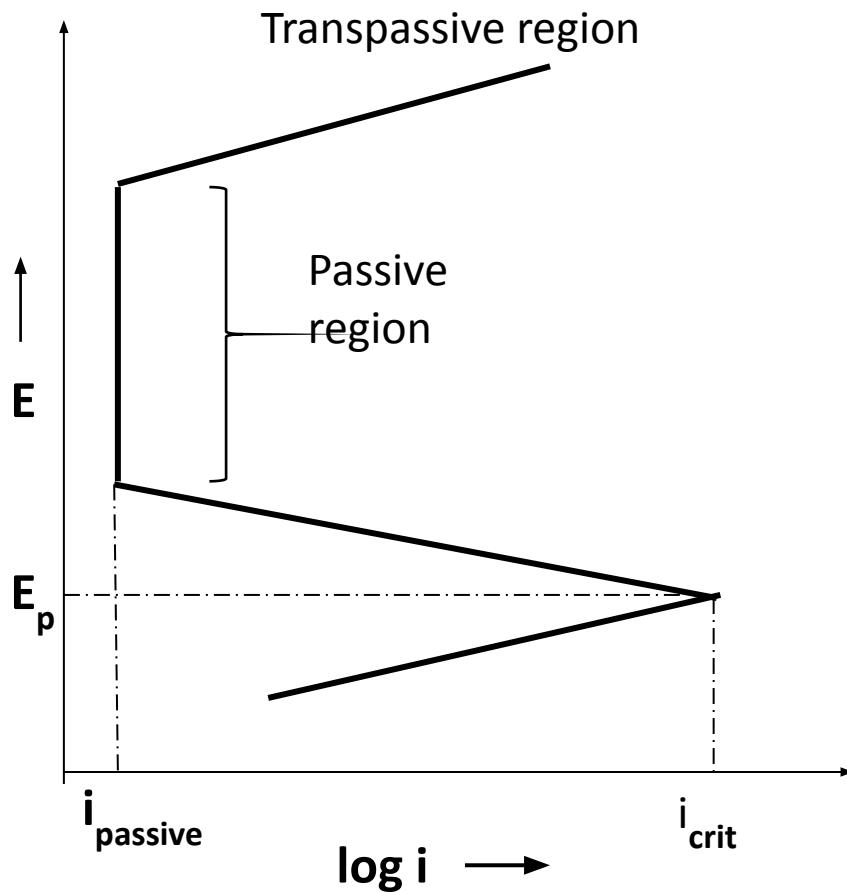
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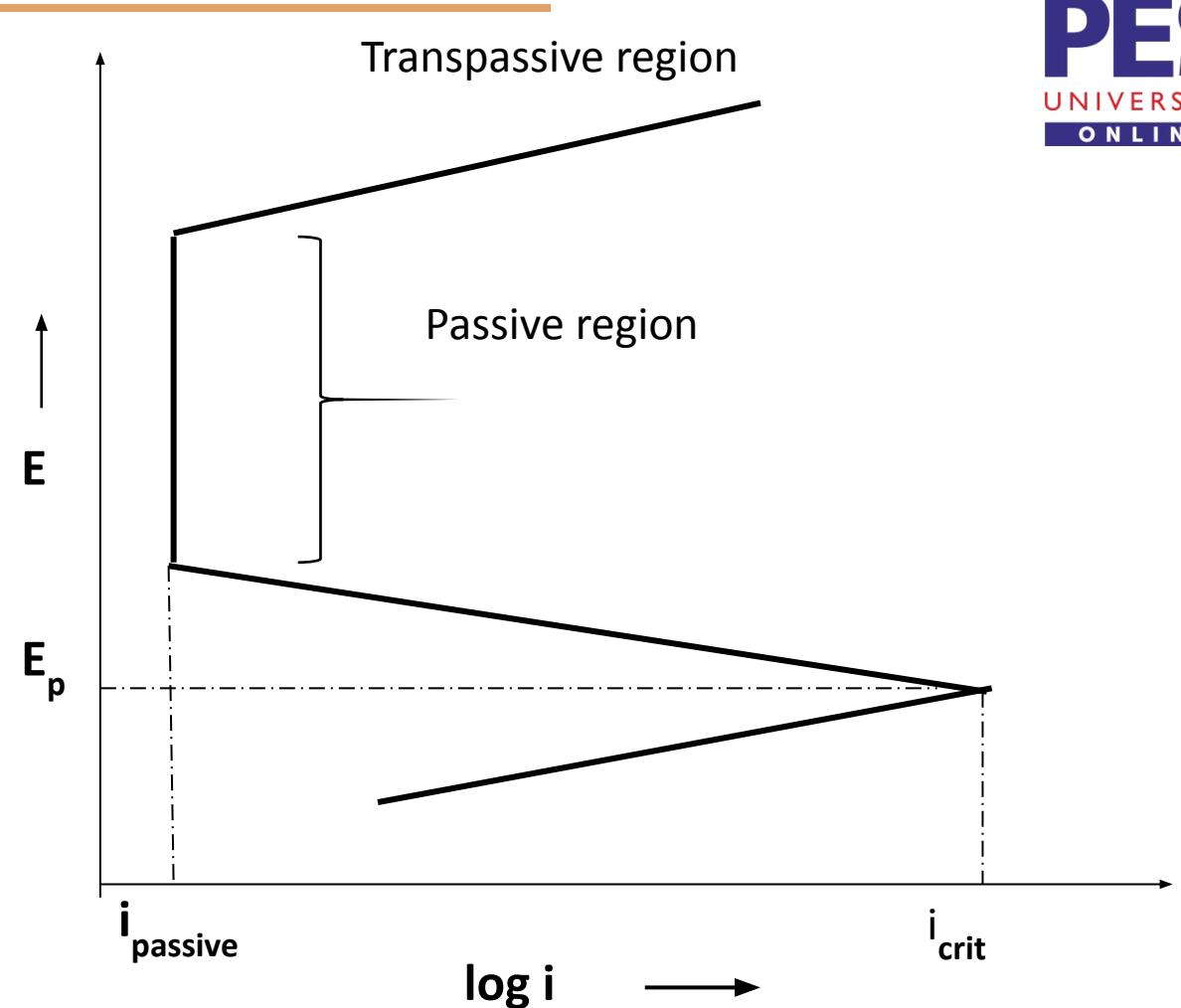
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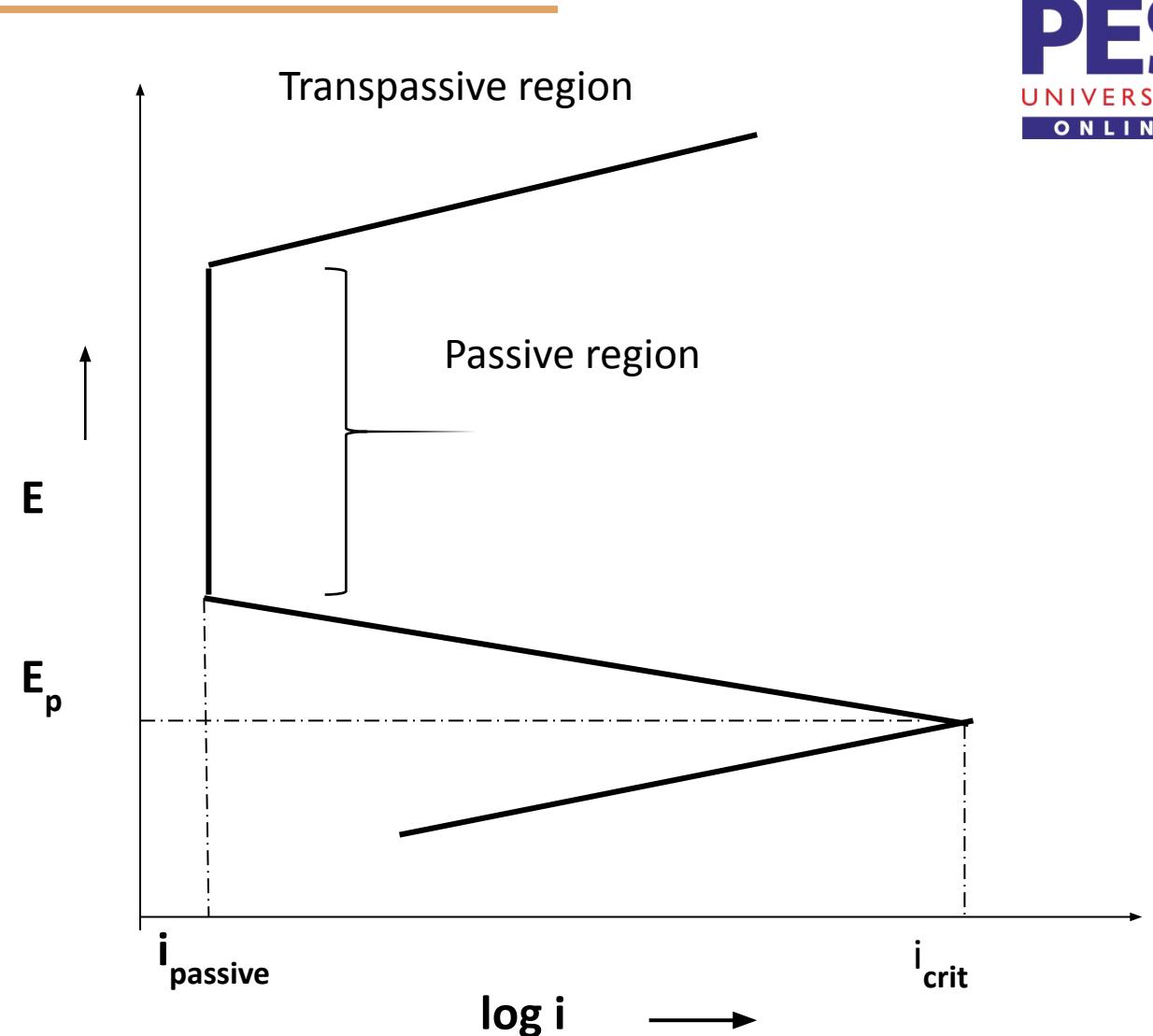
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Anodic protection to a structure is applied by using a device

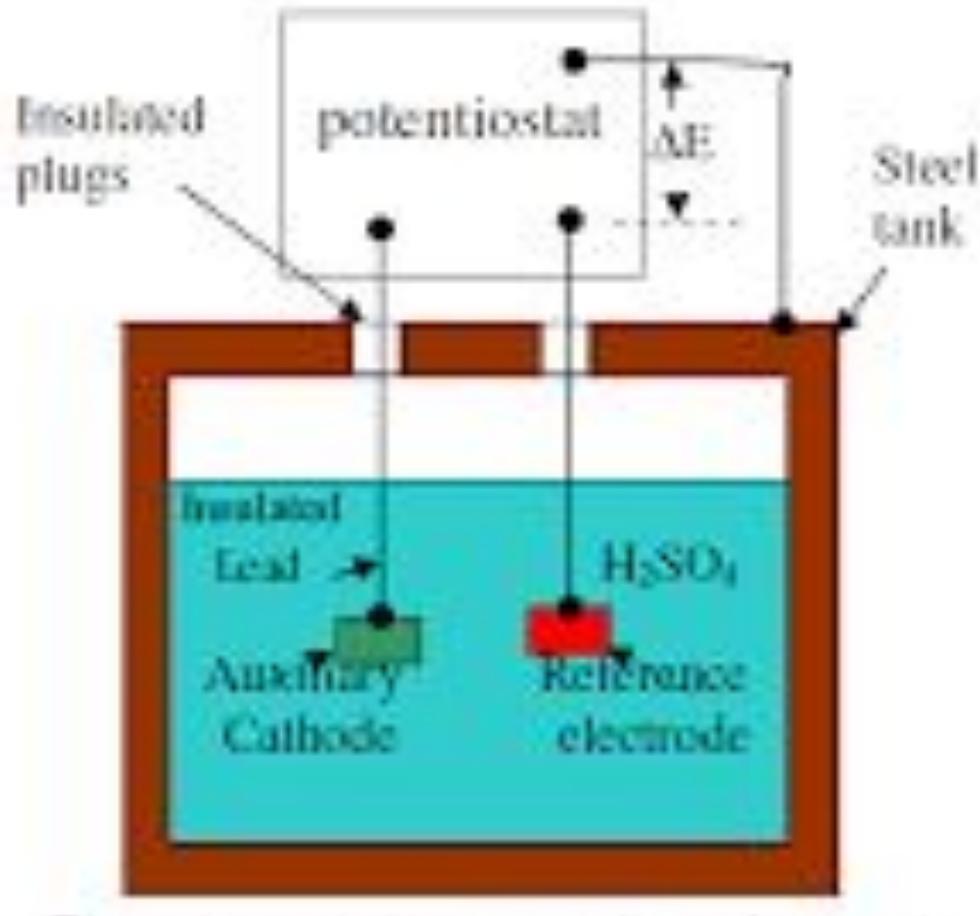
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