



ELECTRO-CHEMICAL CORROSION CHAPTER 3

LECTURER

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Electro-chemical Considerations :

For metallic materials, the corrosion process is normally electrochemical, that is **a chemical reaction** in which there is transfer of **electrons** from one chemical species to another. Metal atoms characteristically lose or give up electrons in what is called an **oxidation reaction**. The site at which oxidation takes place is called the **anode**; oxidation is sometimes called an **anodic reaction**.

The electrons generated from each metal atom that is oxidized must be transferred to and become a part of another chemical species in what is termed **a reduction reaction**. The location at which reduction occurs is called the **cathode**.

Corrosion Cell : For Corrosion to take place ,the information of a corrosion cell is essential. A corrosion cell essentially comprised of the following four components.

- 1) **Anode** .
- 2) **Cathode** .
- 3) **Electrolyte** .
- &
- 4) **Metallic path**.



Anode (-ve of cell): One of the two dissimilar metal electrodes in an electrolytic cell. Electrons are released at anode , which is the more reactive metal .Electrons move through the wire in to the cathode.

Cathode (+ve of cell) :The other Electrode in the electrolytic cell .Reduction takes place at cathode and electrons are consumed .

Electrolyte (e.g. salt solution) : It is the electrically conductive solution for corrosion to occur. Positive electricity passes from anode to cathode through the electrolyte as cations .

Metallic path : The two electrodes are connected externally by a metallic conductor. Current flow from (+) to (-) which really electrons flowing from (- e) to (+e).

Current flow : Conventional current flows from anode (-) to cathode (+) as Zn^{++} ions through the solution. The circuit is completed by passage of electrons from the anode to the cathode through the wire (outer current).

Electron Flow : The circuit is completed by negative ions (-) Which migrate from cathode (+) , through the electrolyte , towards the anode (-).

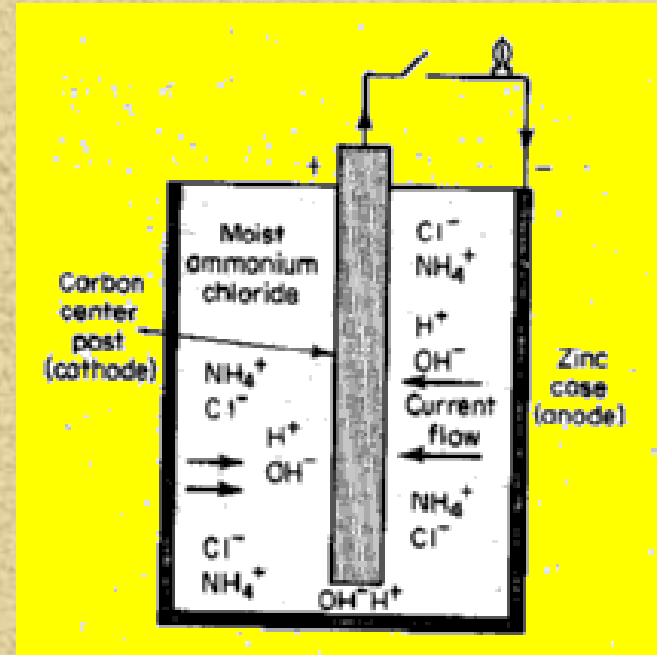
Corrosion



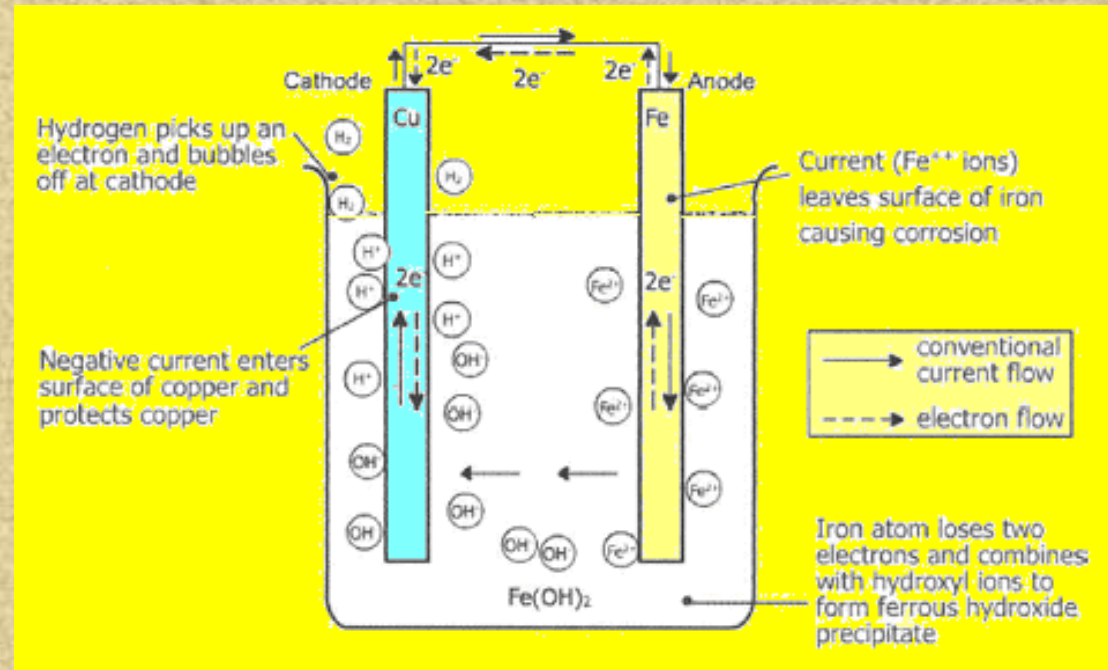
Example :

In the dry Battery
Zinc casing acts as anode.
Carbon electrode acts as cathode.
Moist ammonium chloride acts as
Electrolyte .

e.g. Zn ions dissolve from a zinc
anode and thus carry positive
current away from it ,
through the Aqueous electrolyte.



Anodic And Cathodic Reactions



Anodic reactions characteristics :

- (1) Oxidation of metal to an ion with a charge.
- (2) Release of electrons.
- (3) Shift to a higher valence state.

The process of oxidation in most metals and alloys represents corrosion. If oxidation is stopped, corrosion is stopped.



Cathodic reactions characteristics :

The Process of reductions which occur at the cathode represents protection .Electrons released by the anodic reactions are consumed at the cathode surface. Unlike an anodic reaction , there is a decrease in valence state. (most common Cathodic reactions mentioned above).

Types of Corrosion Cells :

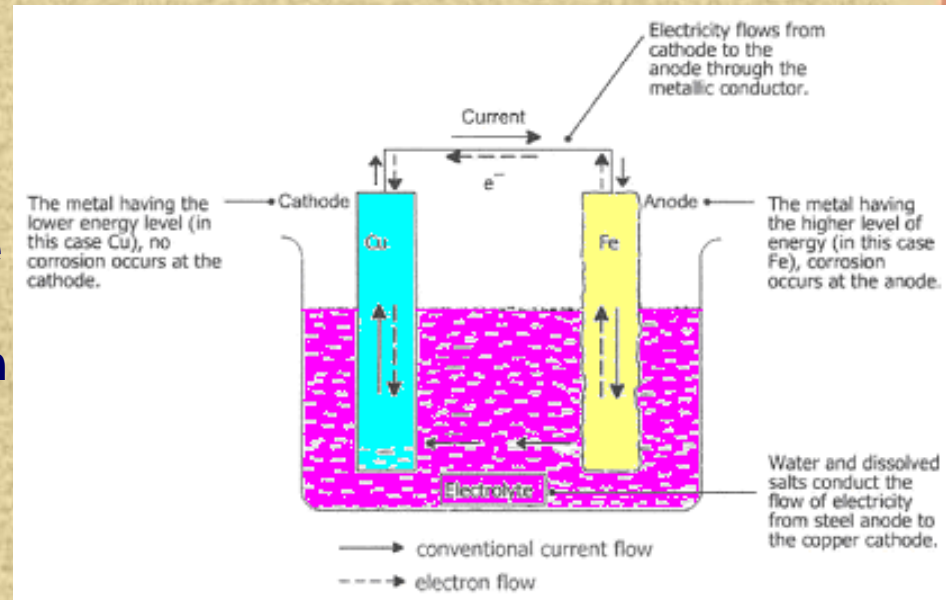
There are several types of corrosion cells:

- (1) Galvanic cells
- (2) Concentration cells
- (3) Electrolytic cell
- (4) Differential temperature cells.



(1) Galvanic cells :

The galvanic cell may have an anode or cathode of dissimilar metals in an electrolyte or the same metal in dissimilar conditions in common electrolyte.



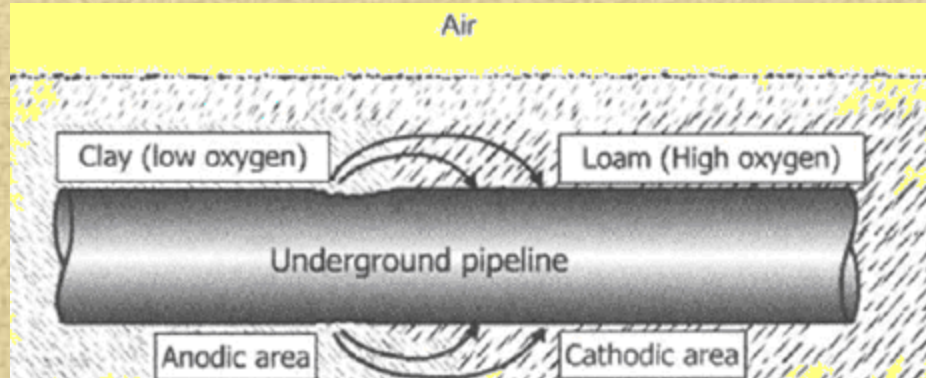
(2) Concentration Cells :

This is similar to galvanic cells except the anode and cathode are of same metals in a heterogeneous electrolyte. A pipe in soil, Concentration cells may be set up by:

- Variation in the amount of oxygen in soils.
- Differences in moisture content of soils.
- Differences in compositions of the soil.

Corrosion

Concentration cells are commonly observed in underground corroding structures, such as buried pipes or tanks.



There are three general types of concentration cell corrosion:

1) Metal Ion Concentration Cells

In the presence of water, a high concentration of metal ions will exist under faying surfaces and a low concentration of metal ions will exist adjacent to the crevice created by the faying surfaces. An electrical potential will exist between the two points. The area of the metal in contact with the low concentration of metal ions will be cathodic and will be protected, and the area of metal in contact with the high metal ion concentration will be anodic and corroded.





2) Oxygen Concentration Cells

A water solution in contact with the metal surface will normally contain dissolved oxygen. An oxygen cell can develop at any point where the oxygen in the air is not allowed to diffuse uniformly into the solution, thereby creating a difference in oxygen concentration between two points. Corrosion will occur at the area of low-oxygen concentration (anode).

3) Active-Passive Cells

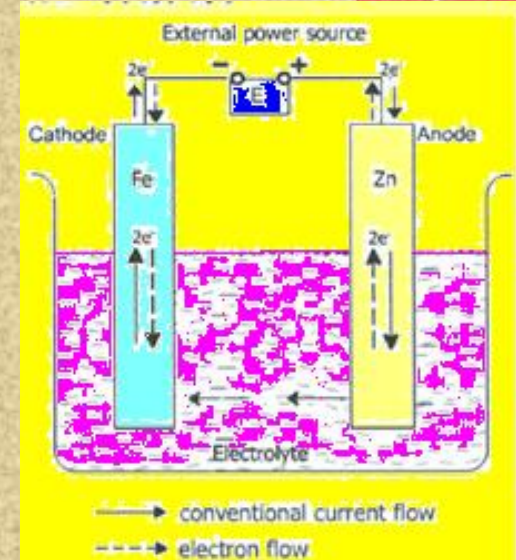
Metals that depend on a tightly adhering passive film (usually an oxide) for corrosion protection; e.g., austenitic corrosion-resistant steel, can be corroded by active-passive cells. The corrosive action usually starts as an oxygen concentration cell; e.g., salt deposits on the metal surface in the presence of water containing oxygen can create the oxygen cell.

The inequality of dissolved chemicals causes a potential difference which establishes anode in the more concentrated region and cathode in the less concentrated region.



(3) Electrolytic Cells :

This type of cell is formed when an external current is introduced into the system. It may consist of all the basic components of galvanic cells and concentration cells plus an external source of electrical energy. Notice that anode has a (+) polarity and cathode has (-) polarity in an electrolytic cell, where external current is applied. This is the type of cell set up for electrically protecting the structures by Cathodic protection. The polarity of an electrolytic cell is opposite to that in a galvanic (corrosion) cell.





(4) Differential Temperature Cells :

This type of cell is formed when two electrode of same metals present in different temperatures , causing in different potential ,high temp. electrode will be the cathode and the lower temp. will be the anode . (e.g. heat exchangers & condensers).

The Electro Motive Series (EMF)

When a metal is immersed in an electrolyte, a dynamic equilibrium is established across the interface with a potential difference between the metal and electrolyte. If a metal is immersed in a solution of its own ions , such as **Zn in ZnSO₄** solution ,or **copper in CuSO₄** the potential obtained is called the reversible potential (E_{rev}) .

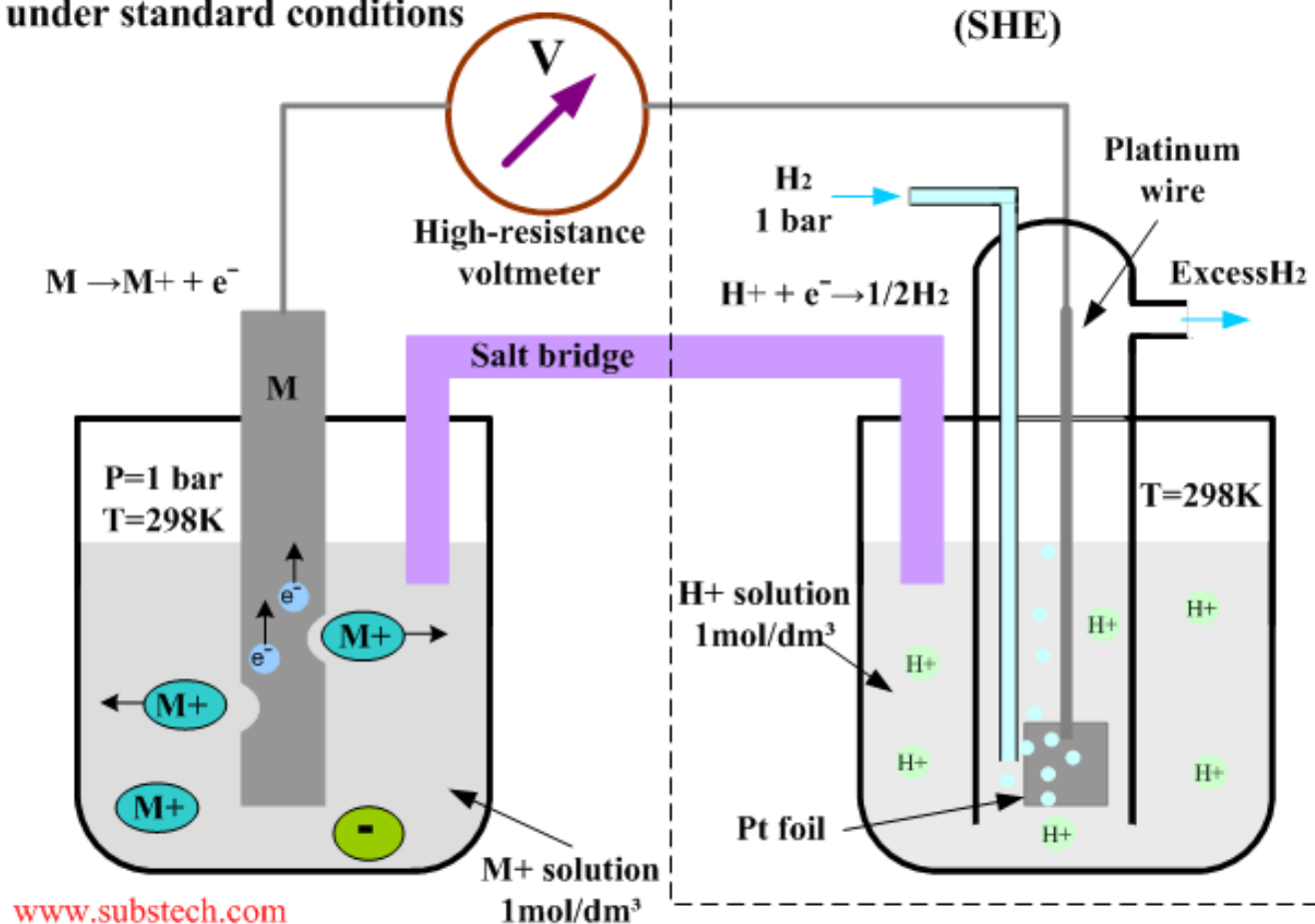
If the metals are in their standard states , such that activities of the metallic ions are equal to unity or gases are at 1 bar pressure , the potentials obtained are called ' Standard Electrode Potentials ' . A standard potential refers to the potential of pure metal measured with reference to a hydrogen reference electrode (H_2 / H^+) which is arbitrarily defined as Zero .It is not possible to establish a reversible potential for alloys containing two or more reactive components , so only pure metals are listed in table below .



Standard electrode potential

Half-cell with metal M electrode
under standard conditions

Standard Hydrogen Electrode
(SHE)



**Table 17.1** The Standard emf Series

	<i>Electrode Reaction</i>	<i>Standard Electrode Potential, V°(V)</i>
	$\text{Au}^{3+} + 3e^{-} \longrightarrow \text{Au}$	+1.420
	$\text{O}_2 + 4\text{H}^{+} + 4e^{-} \longrightarrow 2\text{H}_2\text{O}$	+1.229
	$\text{Pt}^{2+} + 2e^{-} \longrightarrow \text{Pt}$	~+1.2
	$\text{Ag}^{+} + e^{-} \longrightarrow \text{Ag}$	+0.800
	$\text{Fe}^{3+} + e^{-} \longrightarrow \text{Fe}^{2+}$	+0.771
↑ Increasingly inert (cathodic)	$\text{O}_2 + 2\text{H}_2\text{O} + 4e^{-} \longrightarrow 4(\text{OH}^{-})$	+0.401
	$\text{Cu}^{2+} + 2e^{-} \longrightarrow \text{Cu}$	+0.340
	$2\text{H}^{+} + 2e^{-} \longrightarrow \text{H}_2$	0.000
	$\text{Pb}^{2+} + 2e^{-} \longrightarrow \text{Pb}$	-0.126
	$\text{Sn}^{2+} + 2e^{-} \longrightarrow \text{Sn}$	-0.136
	$\text{Ni}^{2+} + 2e^{-} \longrightarrow \text{Ni}$	-0.250
	$\text{Co}^{2+} + 2e^{-} \longrightarrow \text{Co}$	-0.277
	$\text{Cd}^{2+} + 2e^{-} \longrightarrow \text{Cd}$	-0.403
	$\text{Fe}^{2+} + 2e^{-} \longrightarrow \text{Fe}$	-0.440
	$\text{Cr}^{3+} + 3e^{-} \longrightarrow \text{Cr}$	-0.744
	$\text{Zn}^{2+} + 2e^{-} \longrightarrow \text{Zn}$	-0.763
	$\text{Al}^{3+} + 3e^{-} \longrightarrow \text{Al}$	-1.662
	$\text{Mg}^{2+} + 2e^{-} \longrightarrow \text{Mg}$	-2.363
	$\text{Na}^{+} + e^{-} \longrightarrow \text{Na}$	-2.714
↓ Increasingly active (anodic)	$\text{K}^{+} + e^{-} \longrightarrow \text{K}$	-2.924

Corrosion



Galvanic series : In actual corrosion problems , galvanic coupling between metals in equilibrium with their ions rarely occurs. In general , the positions of metals and alloys in the galvanic series agree closely with their constituent elements in the emf series .

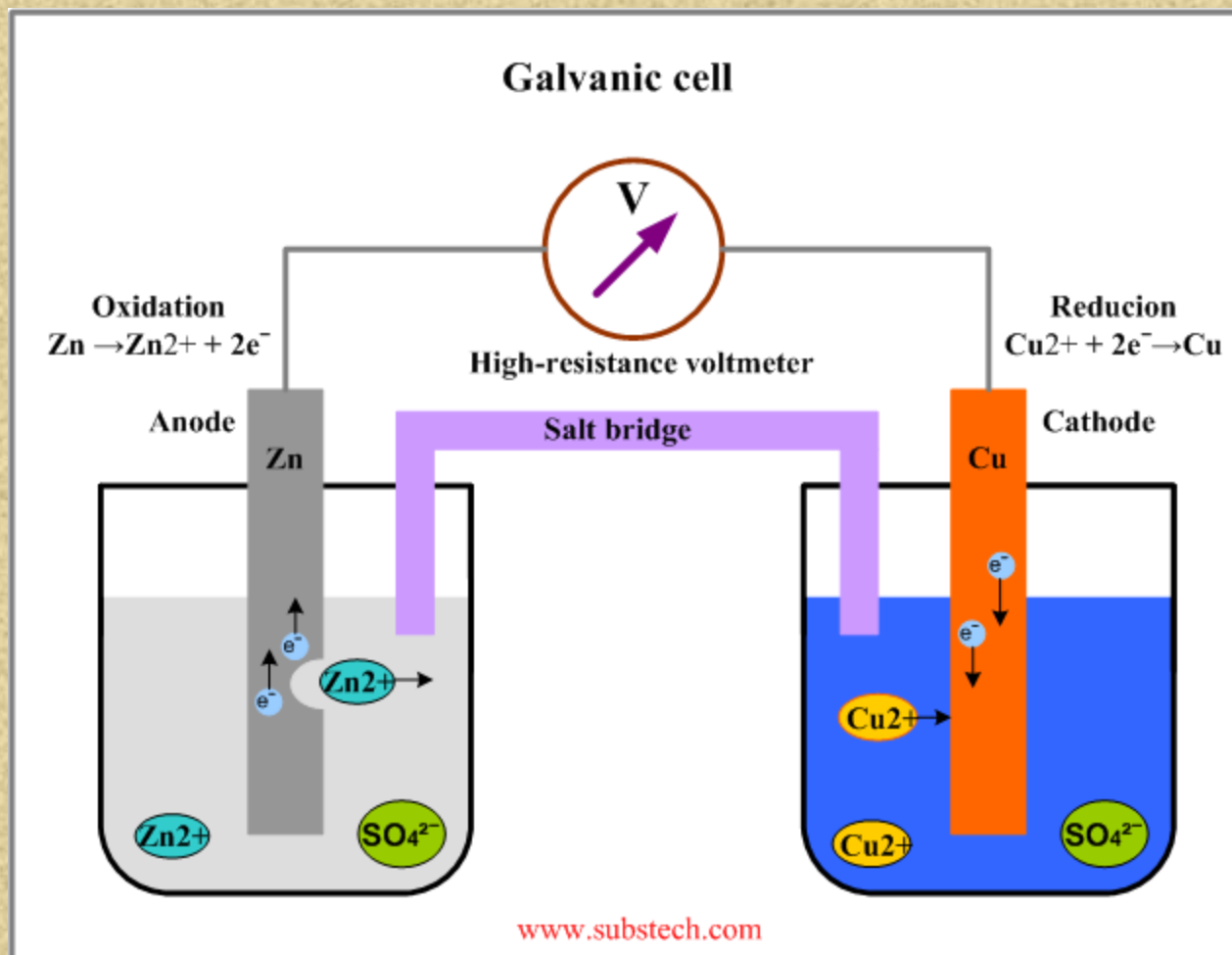
This represents the relative reactivities of a number of metals and commercial alloys in seawater.

Table 17.2 The Galvanic Series

	Platinum
	Gold
	Graphite
	Titanium
	Silver
	[316 Stainless steel (passive)
	[304 Stainless steel (passive)
	[Inconel (80Ni-13Cr-7Fe) (passive)
	[Nickel (passive)
	[Monel (70Ni-30Cu)
	Copper-nickel alloys
	Bronzes (Cu-Sn alloys)
	Copper
	Brasses (Cu-Zn alloys)
	[Inconel (active)
	[Nickel (active)
	Tin
	Lead
	[316 Stainless steel (active)
	[304 Stainless steel (active)
	[Cast iron
	[Iron and steel
	Aluminum alloys
	Cadmium
	Commercially pure aluminum
	Zinc
	Magnesium and magnesium alloys

↑
Increasingly inert (cathodic)

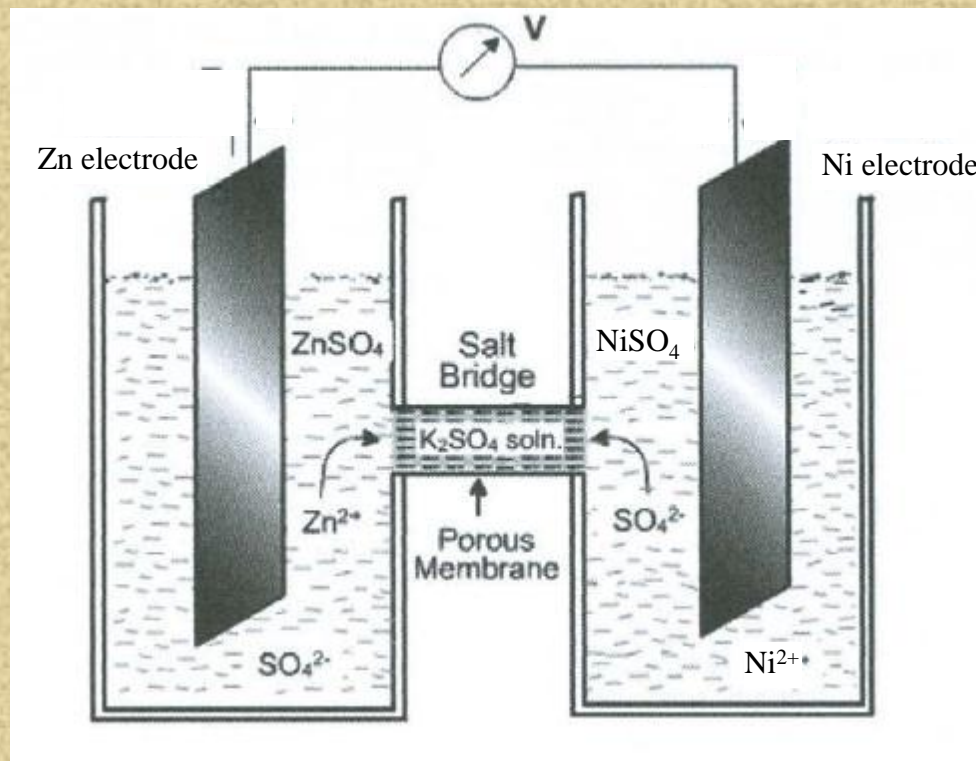
↓
Increasingly active (anodic)



Corrosion

Example 1 : A galvanic cell consist of (Zn) electrode in(ZnSO_4) solution with (1 mole) concentration . The other is of (Ni) electrode in (NiSO_4) solution with (1 mole) concentration . The two electrodes are separated with porous partition to prevent mixing of the two solutions . The two electrodes are contacted with conductive wire . Find.

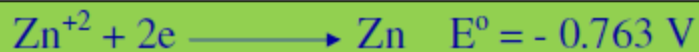
- On which electrode the oxidation reaction will be .
- Which electrode will be the anode .
- Which electrode will corroded .
- what is the EMF for this galvanic cell , circuit close.





Solution :

The half cells reactions are :



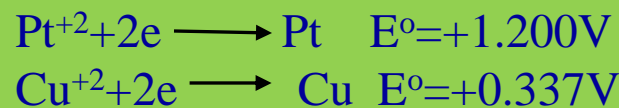
- Oxidation reaction will take place on Zn electrode .Because the potential difference in Zn half cell more negative (- 0.763 V) compare with (-0.250 V) for Ni half Cell .
- From previous answer, Zn electrode is the anode , because the oxidation reaction take place on anode electrode.
- In galvanic cell , the anode electrode is the corroded electrode , for that Zn electrode will corroded.
- Cell potential is the sum of the two half cells potential.



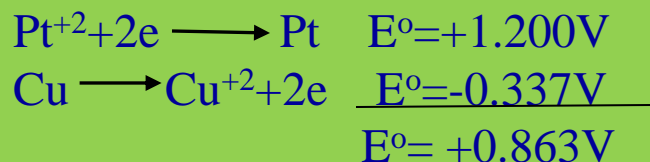
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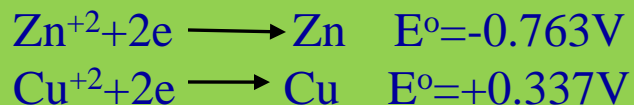
The result of the Cell reaction . Ni potential changed with respect to standard potential cell .This is due to its potential in the EMF series . Also if we connect Pt electrode with Cu electrode we get :



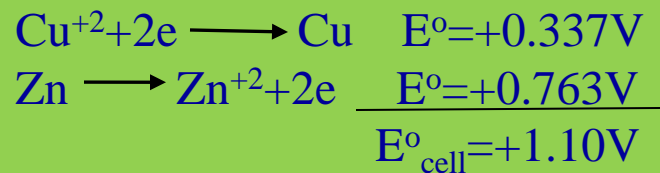
By subtraction the lower potential from the higher we get



If the galvanic Cell contain two electrodes , One of them with (- ve) potential and the other with (+ ve), such as Zinc with Copper .



In this case ,if we subtract Cu potential from Zn potential the result is :



We change reduction sign to get the cell potential difference .

Corrosion



Example 2 : Write the reactions of the anodic half cell (oxidation) and Cathodic half cell (reduction) . For the following electrodes and electrolytes , by using standards potential values :

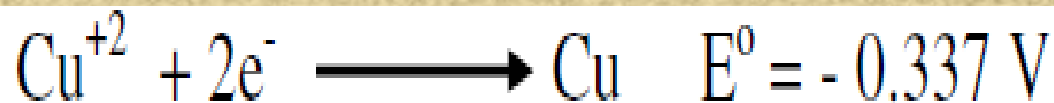
- (a) Zinc and copper electrodes are immersed in dilute (CuSO_4).
- (b) Copper electrode is immersed in water saturated with oxygen.
- (c) Iron electrode is immersed in water saturated with oxygen.
- (d) Magnesium electrode is immersed in water saturated with oxygen.

Solution :

(a)



Oxidation (Anodic reaction)



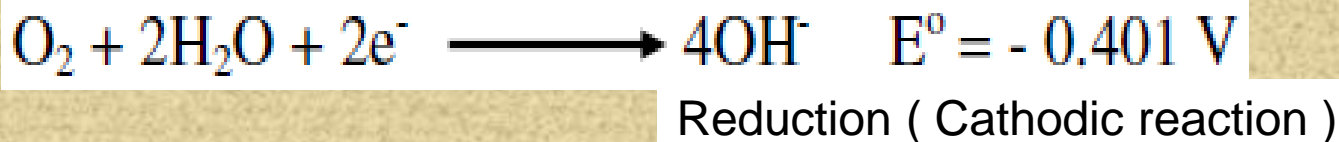
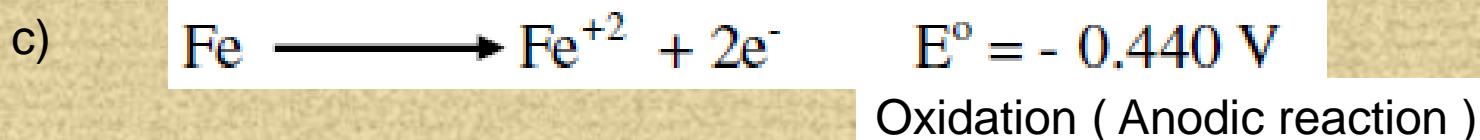
= Reduction (Cathodic reaction)

Changing the sign of Cathodic reaction , we observed that Zinc reaction possess more negative , so it is the anode and oxidation reaction occurred on it.

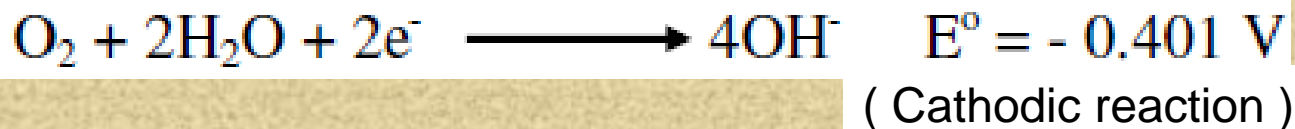
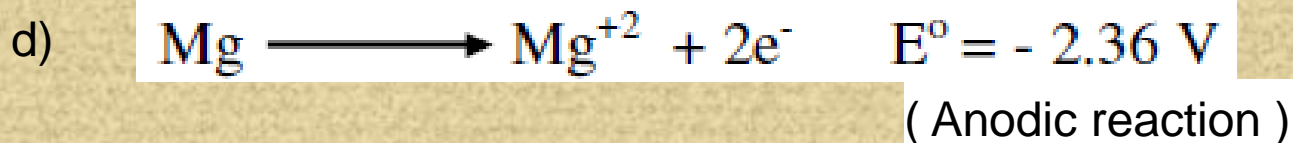
Corrosion



b) May be there is a low rate corrosion or may be there is no corrosion , because the potential difference between Cu oxidation (0.337 V) and that formed in water from hydroxide ion (0.401 V) is very small .



Iron potential's difference is more negative, so it is the anode and oxidation reaction occurred on it.



Mg is more negative in potential, so it is the anode and oxidation reaction occurred on it.



Galvanic Cell with Electrolytes that are not one molar :-

Most of electrolyte solutions of the real galvanic cells are not to be (1 mole) .But they are always dilute solutions , which they are less than (1 mole) .If the ions concentrates in the electrolyte surround to the anode electrode is less than 1 mole , the reaction motive force to dissolve or corrode the anode will be higher .Because there is less concentrate of ions that causes the reverse reaction .There for it will be more negative of electro-chemical series on the anodic half cell.



Truly the metal ion concentration effects (C_{ion}) on the standards potential of the electrochemical series (E°) at (25°) Temperature are given by Nernst equation for the half anodic cell reaction .Where there is one kind of ions are produced . Nernst equation can be written as follow :

$$E = E^{\circ} + \frac{RT}{nF} \ln \left[\frac{a_{\text{products}}}{a_{\text{reactives}}} \right]$$

$$E = E^{\circ} + 2.3 \frac{8.3 \text{ J/K}^{\circ} \cdot \text{mole} \times (25 + 273) \text{ K}^{\circ}}{n \times 96,500 \text{ coulomb}} \log C_{ion}$$

$$E = E^{\circ} + \frac{0.0592}{n} \log C_{ion}$$

Corrosion



Where are :

E = New electrochemical potential for the half cell .

E° = standard electrochemical potential for the half cell .

n = No. of electrons transferred (the valence) .

C_{ion} = molar concentrations of the ions .

R = gas constant = $8.3 \text{ J/K}^\circ/\text{mole}$.

T = Temperature = $25 + 273 = 298 \text{ K}^\circ$.

F = Faraday constant = $96,500 \text{ coulomb}$.

For the Cathodic reaction , the final potential sign must be inverses .

Example 3:

A galvanic cell in (25 C°) temp. it is formed from Zinc electrode in (0.10 mole ZnSO_4) solution , the other electrode is of Nickel in (0.05 mole NiSO_4) solution .The two electrodes are separated with porous wall and connected with external wire. What is the value of the cell potential, when the circle is connected

Corrosion

Solution :

First we suppose that the solutions are in (1 mole) concentrate. So the potentials of Zn & Ni be in standard value of EMF serious . Zn electrode will be the anode because its potential(- 0.763 v) is more negative in the electrochemical cell of Zn – Ni Than of Ni (- 0.250 v).

Then using Nernst equation to correct the potentials of the cell .

$$E = E^{\circ} + \frac{0.0592}{n} \log C_{\text{ion}}$$

$$\begin{aligned} \text{Anode reaction} \quad E_A &= -0.763 \text{ V} + \frac{0.0592}{2} \log 0.10 \\ &= -0.763 \text{ V} - 0.296 \text{ V} \\ &= -0.793 \text{ V} \end{aligned}$$

$$\begin{aligned} \text{Cathodic reaction} \quad E_C &= -(-0.250 \text{ V} + \frac{0.0592}{2} \log 0.05) \\ &= +0.250 \text{ V} + 0.0385 \text{ V} \\ \text{emf of Cell} = E_A + E_C &= -0.793 \text{ V} + 0.288 \text{ V} \\ &= -0.505 \text{ V} \end{aligned}$$

In the modern theory principles we shall take the free energy to solve Nernst equation .





$$\text{No. of moles} = \frac{\text{weight in gm}}{\text{atomic weight in gm/mole}}$$

$$\text{Molarity (M)} = \frac{\text{moles of solute}}{\text{litter of solution}}$$

$$\begin{aligned} \text{Unit activity [a]} &= \frac{1 \text{ gram atomic weight of metal ions}}{\text{litter}} \\ &= M \times \gamma \end{aligned}$$

γ is the activity coefficients.



$$E = E^{\circ} + \frac{R T}{n F} \ln \frac{[a \text{ reactants}]}{[a \text{ products}]}$$



$$E = E^{\circ} - \frac{R T}{n F} \ln \frac{[a \text{ reactants}]}{[a \text{ products}]}$$

Corrosion

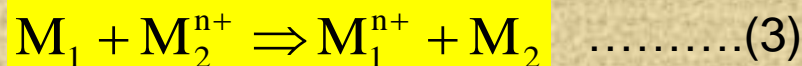


Electrochemical cell potential for two standard half-cells that are electrically coupled

Consider the generalized reactions involving the oxidation of metal M_1 and the reduction of metal M_2 as

$$M_1 \Rightarrow M_1^{n+} + n e^- \quad - E_1^\circ \quad \dots\dots\dots(1)$$


Where the E° s are the standard potentials as taken from the standard emf series. Since metal M is oxidized, the sign of E_1° is opposite to that as it appears in Table of standard emf the two above equations yields.



And the cell potential ΔE° is

$$\Delta E^\circ = E_2^\circ - E_1^\circ \quad \dots\dots\dots(4)$$

For this reaction to occur spontaneously, ΔE° Must be positive ;if it is negative, The spontaneous cell direction is just the reverse of equation(3) . When standard half-cell are coupled together, the metal that lies lower in emf table will experience oxidation (i.e., corrosion), whereas the higher one will be reduced.



Influence of Concentration and Temperature on Cell Potential

Nernst equation electrochemical cell potential for two half-cells that are electrically coupled and for which solution ion concentrations are other than 1M.

$$\Delta E = (E_2^{\circ} - E_1^{\circ}) - \frac{RT}{nF} \ln \left[\frac{M_1^{n+}}{M_2^{n+}} \right] \dots\dots\dots(5)$$

Simplified form of Eq. (5) for T = 25°C (room temperature).

$$\Delta E = (E_2^{\circ} - E_1^{\circ}) - \frac{0.0592}{n} \log \left[\frac{M_1^{n+}}{M_2^{n+}} \right]$$