

## Unit IV Corrosion Chemistry

### Corrosion

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## Unit IV Corrosion Chemistry

**Corrosion** is defined as the destruction or deterioration and consequent loss of metals by direct chemical attack or electrochemical attack by the environment.

Example: (i) Rusting of iron – a reddish brown scale formation on iron and steel objects. It is due to formation of hydrated ferric oxide.

(ii) Green scales formed on copper vessels. It is due to the formation of basic cupric carbonate.  
( $\text{CuCO}_3 + \text{Cu}(\text{OH})_2$ )

### Why do metals undergo corrosion?

Most metals, except the noble metals, occur in nature in the form of their compounds such as oxides, sulfides, carbonates, chlorides, etc. The metals are extracted from these ores by reduction. The extraction of metals from their ores is an endothermic process, energy being supplied in the form of heat or electrical energy. Consequently, 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. Therefore, when metals are put use in various forms, they combine with constituents of the environment and get converted into their compounds. Thus corrosion of metals can be considered as extractive metallurgy in reverse. They always want to be in the stable state; hence it gets oxidized and come back to its original state by oxidation process called corrosion.

### Classification of Corrosion:

**Dry corrosion (Chemical corrosion):** If the corrosion of metal takes place in the absence of moisture is called dry corrosion.

Chemical corrosion occurs due to the direct chemical reaction between the metal and the gases present in the corrosion environment. This type of corrosion is generally observed in the absence of moisture or a conducting electrolytic medium and therefore, known as dry corrosion. Direct oxidation of metals and alloys on exposure to oxygen in air is a common example of chemical corrosion. Apart from oxygen many corrosive gases such as  $\text{HCl}$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{Cl}_2$ ,  $\text{F}_2$ , etc., also react with the metal and alloy surfaces when they come in contact with them.

**Wet corrosion:** If the corrosion of metal takes place by direct electrochemical attack or in the presence of moisture is called wet corrosion.

### Electrochemical theory of corrosion:

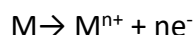
**According to electrochemical theory,** a large number of tiny galvanic cells are formed due to the formation of separate anodic and cathodic regions on the metal surface or when the two different metals are in contact with each other in the presence of a conducting medium. At the anodic region oxidation reaction takes place and the metal gets converted into its ions, liberating electrons. Therefore metal undergoes corrosion at the anodic region. At the cathodic region, reduction reaction

takes place. Since the metal cannot be reduced further, metal atoms at the cathodic region are unaffected by the cathodic reaction.

The electrons liberated at the anodic region migrate to the cathodic region constituting corrosion current. The metal ions are formed at the anode, some anions are formed at the cathode, and they diffuse towards each other through the conducting medium and form a corrosion product somewhere between the anode and the cathode. Corrosion of metal continues as long as both anodic and cathodic reactions take place simultaneously. There cannot be an anodic reaction without a cathodic reaction and vice versa.

**Anodic reaction** is a simple oxidation reaction in which the metal atoms are converted into their ions, liberating electrons.

At the anodic region:



For example, when iron undergoes corrosion,

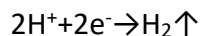


But the cathodic reactions are more complicated than anodic reactions as the constituents of the corrosion medium are involved in the reaction, and are dependent on the nature of the corrosion environment. The most common types of cathodic reactions are either liberation of hydrogen or absorption of oxygen. Correspondingly, the corrosion types are known as hydrogen type corrosion and oxygen type corrosion.

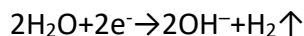
At the cathodic region:

**(a) Liberation of hydrogen takes place in the absence of oxygen.**

(i) In the acidic medium and in the absence of oxygen, the cathodic reaction is,

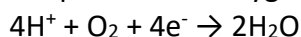


(ii) In neutral or alkaline medium and in the absence of oxygen, hydroxide ions are formed with simultaneous liberation of hydrogen.

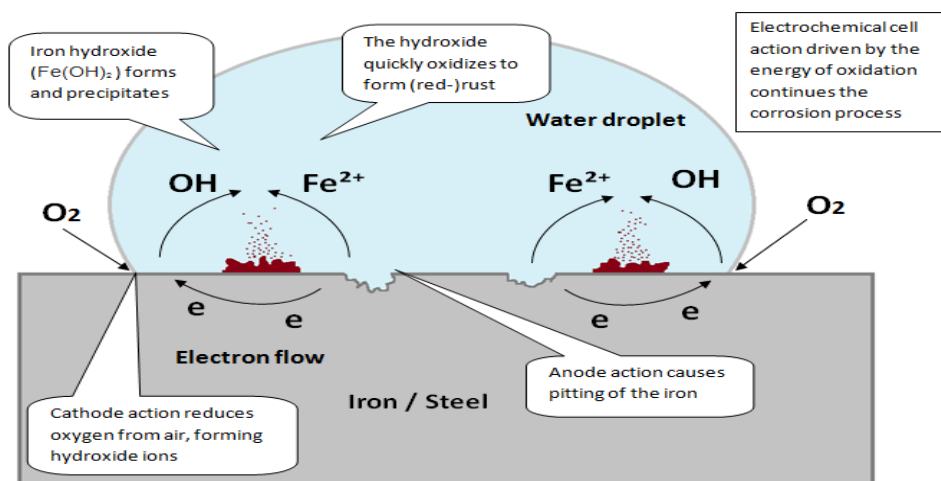
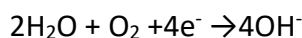


**(b) Absorption of oxygen takes place in the presence of oxygen.**

(i) In the acidic medium and in the presence of oxygen.

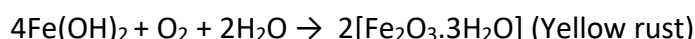
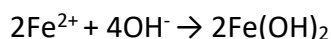


- (ii) In neutral or alkaline medium and in the presence of oxygen, hydroxide ions are formed by the following reaction.



Source : [https://www.fabory.com/knowledge\\_center/technical/surface\\_treatments](https://www.fabory.com/knowledge_center/technical/surface_treatments)

- Corrosion of iron produces  $\text{Fe}^{2+}$  ions and  $\text{OH}^-$  ions at the anode and cathode sites respectively. These ions diffuse towards each other. Since smaller  $\text{Fe}^{2+}$  ions diffuse more rapidly than  $\text{OH}^-$  ions, their combination occurs more commonly near the cathodic region to produce insoluble  $\text{Fe}(\text{OH})_2$ . In an oxidizing environment, it is oxidized to ferric oxide and the yellow rust is hydrated ferric oxide.



In the presence of limited oxygen, ferrous hydroxide is converted into magnetic oxide of iron ( $\text{Fe}_3\text{O}_4$ ) and is known as black rust.



## Types of corrosion:

- Differential metal corrosion
- Differential aeration corrosion
- Stress corrosion

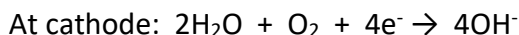
### 1. Differential metal corrosion or Galvanic corrosion:

This type of corrosion occurs 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.

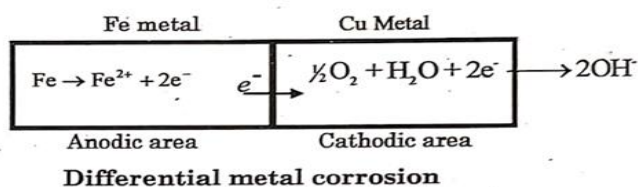
The anodic metal undergoes oxidation and gets corroded. The cathodic metal undergoes reduction and remains unaffected.

The reactions may be represented as follows:

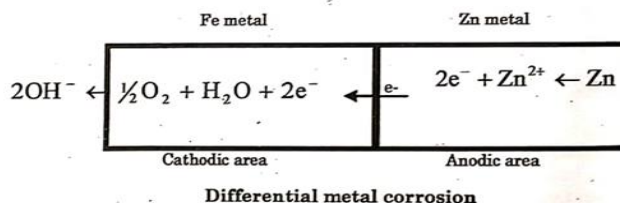


Examples:

- a) Standard electrode potential of Fe (-0.44 V) is less than that of Cu (0.34 V). Therefore, when iron is in contact with copper, iron becomes anodic and undergoes corrosion, whereas copper becomes cathodic and remains unaffected.



- b) Standard electrode potential of Zn (-0.76 V) is less than that of Fe (-0.44 V). Therefore, when iron is in contact with zinc, Zn becomes anodic and undergoes corrosion. Fe becomes cathodic and remains unaffected.



- c) Steel screws/rivets in copper sheet  
d) Steel pipe connected to copper plumbing  
e) Lead antimony solder around copper wire

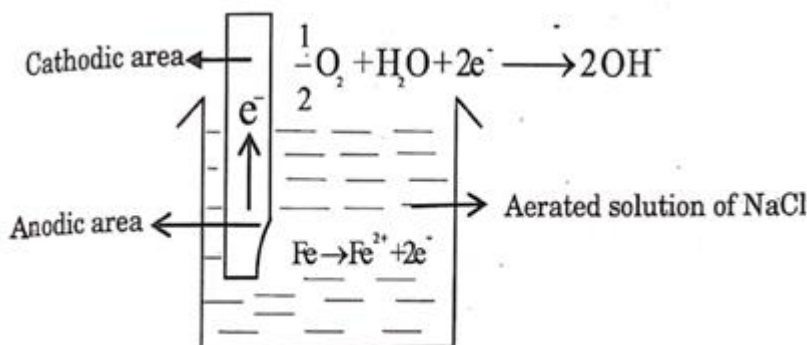
**Galvanic Series:** Although iron shows a tendency undergo corrosion its alloy stainless steel shows a good corrosion resistance. Aluminium metal has a tendency to get oxidized but gets passivated due to the formation of oxide film. Hence electrochemical series is not totally sufficient to explain the corrosion behavior of all metals. In fact alloys are not included in this series. Hence another series named galvanic series has been prepared that contains commercial metals and alloys were arranged in the order of their corrosion tendencies or corrosion resistance.

## 2. Differential aeration corrosion:

When a metal is exposed to different concentration of air ( $O_2$ ), part of the metal exposed to lower concentration of  $O_2$  will have lower potential, and hence becomes anodic and

undergoes corrosion. Other part of the metal exposed to higher concentration of oxygen and hence becomes cathodic and remains unaffected. The difference in oxygen concentration produces a potential difference and cause corrosion current to flow. This type of corrosion is called differential aeration corrosion.

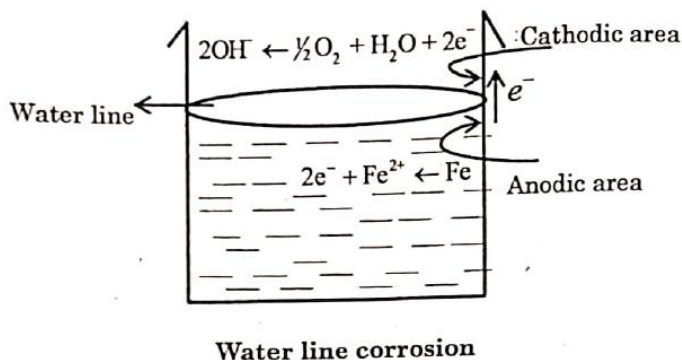
Example: Iron rod partially dipped in NaCl solution



**Waterline corrosion:** It is observed in Ships floating in sea water for long time. Or the part of the metal immersed in half filled water tank.

When a steel tank is partially filled with water for a long time, the inner portion of the tank below the water line is exposed only to dissolve oxygen, whereas, the portion above the water line is exposed to more oxygen. Thus the portion below the water line acts as anode and undergoes corrosion. The upper portion acts as cathode and remains unaffected.

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



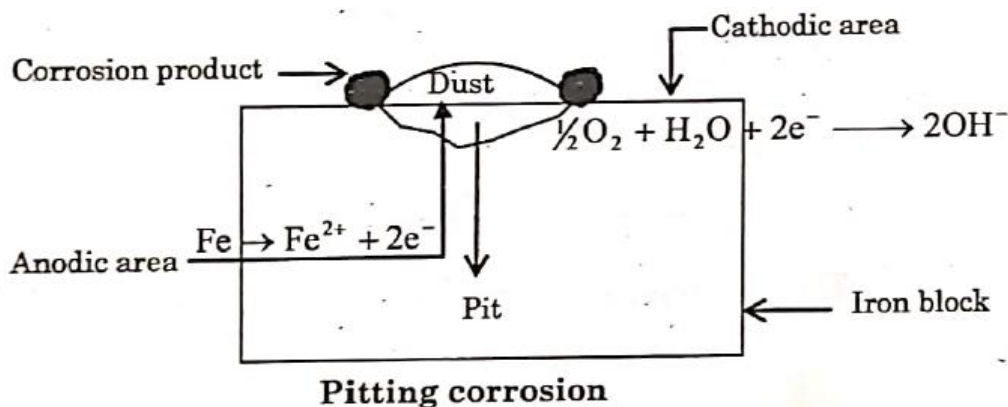
## Pitting Corrosion:

Pitting corrosion is a localized and accelerated corrosion, resulting in the formation of pits or pin holes, around which the metal is relatively unattacked. Pitting is one of the most destructive forms of corrosion.

Pitting corrosion is observed 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 and undergoes corrosion. Thus, metal is lost underneath the surface of dust particle forming a deep and narrow pit.

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The adjacent area of the metal which is exposed to higher concentration of  $O_2$  becomes cathodic and remains unaffected.

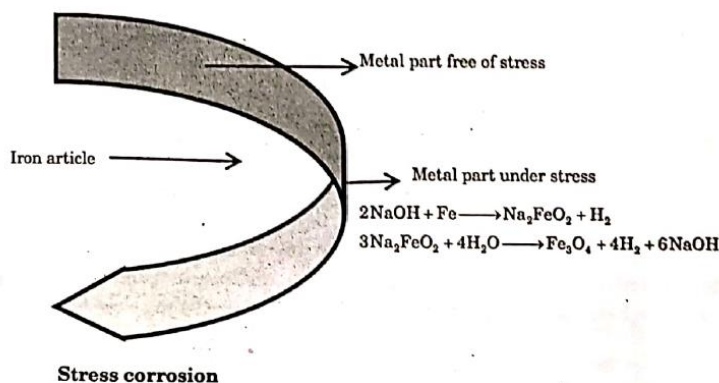


Pitting corrosion is characterized by small anodic area and large cathodic area, resulting in accelerated corrosion at the anodic area. Pitting corrosion is also caused by the break down of the protective film on a metal surface.

For example, peeling off of a small tin coating on iron gives rise to a small anodic area and large cathodic area.

### 3. Stress Corrosion:

Stress corrosion is a type of corrosion that occurs when some part of the metallic material is under stress and exposed to specific corrosive environment. The stress can be applied stress or residual stress or both.



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 also be external stress acting on the metal during service conditions. The metal atoms under stress are always at higher energy levels as compared to the ones free from stress. The stressed part of the metal 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. Under specific corrosive environments the stressed part undergoes corrosion, initiating the crack.

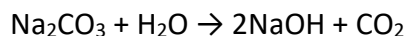
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The presence of both tensile stress and corrosive environment are necessary for stress corrosion to occur. Alloys are more susceptible for stress corrosion than pure metals. For example, brass undergoes stress corrosion in the presence of ammonia and stainless steel in the presence of chloride ions and caustics.

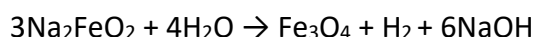
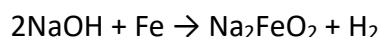
### Caustic embrittlement of boilers:

Caustic embrittlement is the phenomena in which the material of the boilers becomes brittle due to the accumulation of caustic soda.

- It is a form of stress corrosion that occurs in boilers at high pressure leading to the failure of the boiler.
- Steam boilers are made of mild steel plates which are joined together by rivet.
- This is initiated at stressed parts like minute crevices below the rivet, cracks, joints, bends etc.
- In case of high pressure boilers, excess of sodium carbonate is added during the process of removal of hardness of water. As a result the boiler feed water is slightly alkaline, which at high pressure decomposes to give sodium hydroxide.



The NaOH formed flows into hairline cracks, crevices between rivets and joints through capillary action. Inside the cracks and crevices water gets evaporated leaving behind NaOH. The concentration of NaOH gradually increases on these sites due to poor circulation of water. When the concentration of NaOH reaches a value of 10 %, it reacts with stressed region of the metal (iron) and forms sodium ferrate ( $\text{Na}_2\text{FeO}_2$ ) which decomposes to give  $\text{Fe}_3\text{O}_4$  and NaOH.



NaOH thus formed, further reacts with iron to cause stress corrosion cracking. Cracks are produced along intergranular path which sometimes is accompanied by 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)**

The iron in contact with concentrated NaOH, being under stress, becomes anode, while stress free iron surrounded by dilute NaOH becomes cathode. The anodic region undergoes corrosion leading to crack propagation which may result in boiler failure.



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This can be prevented by the addition of compounds such as sodium sulfate, tannin, lignin, phosphates, etc., which block the cracks or crevices, thereby preventing the infiltration of alkali.

### Factors affecting the rate of corrosion:

- a) **Nature of the metal:** The metals with lower electrode potential values are more reactive than the metals with higher electrode potential values. The more reactive metals are more susceptible for corrosion. Thus the tendency of the metal to undergo corrosion decreases with increase in electrode potential.

**Ex:** 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.

- b) **Difference in potential between anodic and cathodic region:** Larger the potential difference between the anodic and cathodic regions, higher is the rate of corrosion. When potential difference is more, higher corrosion current is produced and 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. For example, the potential difference between iron and copper is 0.78 V, and between iron and tin is 0.3 V. Therefore, corrosion is faster when iron is in contact with copper.

The use of dissimilar metals should be avoided wherever possible. Otherwise, the anodic metal gets corroded.

- c) **Nature of the corrosion product:** The corrosion product formed on the surface of the metal may or may not act 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.

On the other hand 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 surface takes place continuously.

Example: Oxides of aluminium, chromium, titanium, etc, acts as protective film whereas iron, zinc, magnesium, etc., do not form any protective film on the surface of the metal.

- d) **The ratio of anodic to cathodic area:** The rate of corrosion is greatly influenced by the relative sizes of anodic and cathodic area. If a metal has a small anodic area and large cathodic area(i.e., the ratio of anodic to cathodic area is small), then the corrosion is more intensive and faster is the corrosion rate at the anodic region. As this ratio decreases, the corrosion rate increases rapidly. This is explained as follows. When the anode is smaller and

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cathode is large all the electrons liberated at the anode, are rapidly consumed at the cathode region. This process makes the anodic reaction faster thereby increasing the corrosion rate. If the cathode is smaller, the consumption of electrons will be slower and the corrosion reaction as a whole will be slower. For example, a broken coating of tin on iron surface results in intense corrosion at the broken region. Iron is anodic to tin. Exposed region of iron acts as anode with small area and tin acts as cathode which has large area. Because of small ratio of anodic to cathodic area, the corrosion rate is very high.

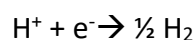
- e) **Hydrogen overvoltage:** Theoretically, certain potential difference between anode and cathode is required for the hydrogen evolution to occur at cathode. But in practice, the potential difference required is more than the theoretical value. This excess potential difference is called hydrogen over voltage.

A metal with low hydrogen overvoltage on its surface is more susceptible for corrosion, when the cathodic reaction is hydrogen evolution type. With lower hydrogen overvoltage, hydrogen gas is liberated easily and thus the cathodic reaction rate is faster. This will make anodic reaction is also faster, thereby promoting overall corrosion reaction. When the hydrogen overvoltage on the metal surface is high, cathodic reaction is slower and the corrosion of the metal also becomes slower.

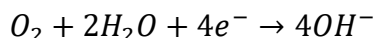
- f) **Temperature:** Rate of corrosion increases with increase in temperature. This is due to the increase in conductance of the medium with increase in temperature and hence an increase in the diffusion rate. As a consequence, corrosion progresses faster at higher temperatures. Rise in temperature also may cause, decrease in viscosity, breakdown of protective film and decrease in polarization which again leads to an increase in the corrosion rate. Increase in the solubility of corrosion product also increases the corrosion rate.

- g) **pH:** In general rate of corrosion is higher in acidic pH than in neutral and alkaline pH i.e. lower the pH more is the corrosion. The reasons are:

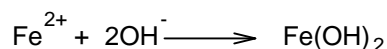
(a) At low pH the concentration of  $[H^+]$  is more, hence the reduction reaction will take place at a faster rate.



If the pH is between 3 to 10, the rate of corrosion depends on the availability of oxygen on the cathodic area for reduction.



If the pH is greater than 10, then corrosion practically ceases due to the formation of insoluble metal hydroxides.



- b) Corrosion product is usually soluble in acidic medium. So as the product is formed it dissolves exposing a new surface.

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But for metals like Aluminium, corrosion rate is high in alkaline medium because protective film gets dissolved in alkali.

h) **Polarization at anodic and cathodic region:**

The difference in potential between anodic and cathodic area is the main driving force for corrosion to occur. Higher the difference in potential, higher is the corrosion current flowing and higher will be the rate of corrosion. The potential of anodic and cathodic areas is greatly influenced by movement of ions on the surface of metal. At anodic area, metal is oxidized, liberating metal ions which move towards cathodic area over the metal surface.

Metal ions liberated at anode cannot move freely towards cathodic area because of opposing factors like lower conductivity and higher resistance of the medium. Thus, metal ions get concentrated at anodic area. This increases the potential of anode and decreases the rate of oxidation. This phenomenon of increasing potential of anodic area due to insufficient movement of ions over the surface of metal is called anodic polarization and the potential is called anodic polarization potential.

Similarly, due to insufficient movement of hydroxyl ions formed at cathodic area towards anodic area, their concentration increases. Cathodic polarization occurs due to the accumulation of hydroxyl ions in the vicinity of cathodic region. This accumulation retards the movement of cathodic reactant (oxygen) towards the cathodic surface. Hence, the rate of cathodic reaction decreases. A retarded cathodic reaction results in retardation of anodic reaction also. Thus the corrosion process is slowed down.

Or

Cathode polarization retards the cathodic reaction. This can be due to chemical polarization of the cathode, i.e., hindering the combination of cathodic reactant with the electron. The retarded movement of the cathodic reactant to the cathode surface or retarded removal of the cathodic reaction product from the surface of the cathode also makes the cathodic reaction slower.

- i) **Electrical conductivity of the corrosion medium:** As the conductivity of the corrosion medium increases, the corrosion rate also increases. Higher the conductivity of the medium, faster the ions can migrate between the anodic and cathodic regions of the corrosion cell, in turn, faster will be the exchange of electrons at the electrode surfaces. This facilitates higher corrosion rate.
- j) **Humidity:** Corrosion rate increases with increase in the humidity in the medium. The presence of moisture in the atmosphere provides the conducting medium for the formation of galvanic cell, facilitating corrosion of the metal.

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### Corrosion Control:

#### (1) Protective coatings

- (i) Metal coating
  - (a) Anodic metal coating (Galvanizing)
  - (b) Cathodic metal coating (Tinning)
- (ii) Inorganic coating - Surface conversion coating
  - (a) Anodizing
  - (b) Phosphating
- (iii) Organic coating

#### (2) Corrosion inhibitors

- (i) Anodic inhibitors
- (ii) Cathodic inhibitors

#### (3) Cathodic protection

- (i) Sacrificial anode method
- (ii) Impressed current method

#### (4) Anodic protection

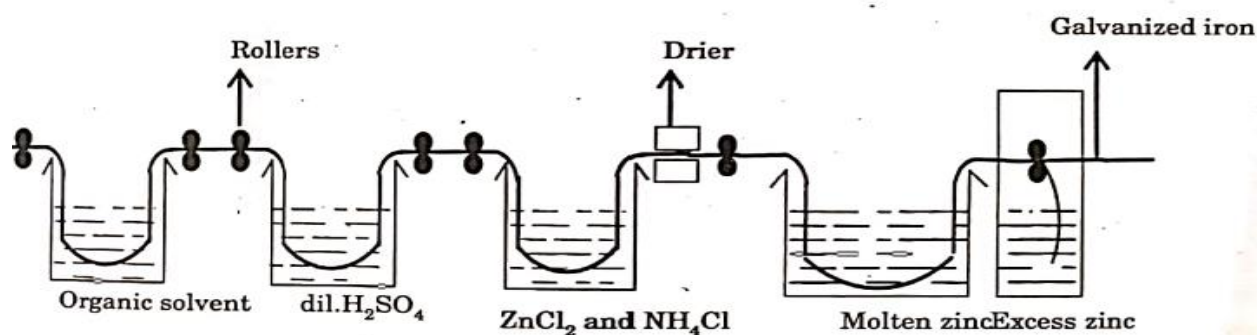
##### (1) Protective coatings:

**(i) Metal coating:** In this case, the 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.

**(a) Anodic metal coating:** It is the coating of a layer of metal which is anodic to base metal. In this type of coating, even if the base metal is not completely covered, it will not undergo corrosion. This is due to formation of large anodic and smaller cathodic area.

**Example:** Coating of Zn or Mg or Cd metal on iron

**Galvanizing:** Coating a layer of zinc on iron by hot dipping is called as galvanization. The following steps are involved in the process,



- 1) Iron sheet is passed through organic solvent to remove oil or grease present on it.
- 2) Then it is washed with dil. H<sub>2</sub>SO<sub>4</sub> to remove any rust (Oxide layer) present on the surface (pickling)
- 3) Then it is treated with a mixture of aqueous solution of ZnCl<sub>2</sub> and NH<sub>4</sub>Cl which acts as flux and then dried.
- 4) Finally it is dipped in molten zinc at 425-430° C.
- 5) Excess zinc present on iron sheet is removed by passing hot rollers.

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

## Note:

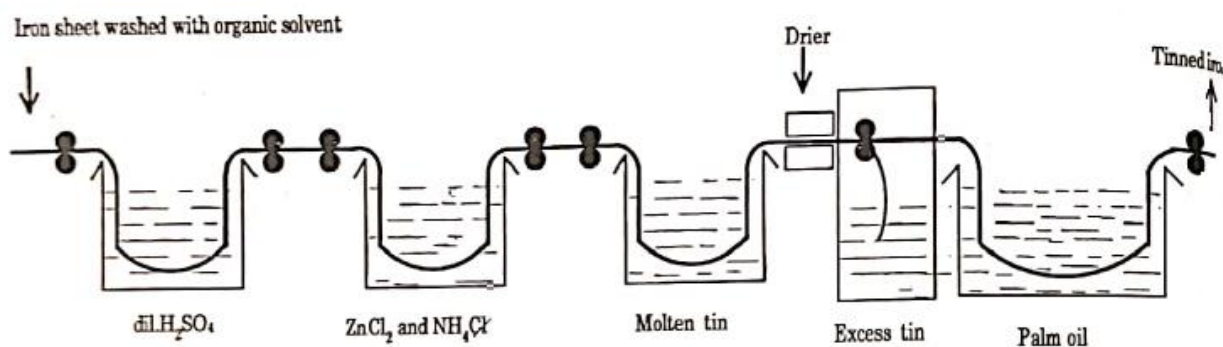
- Even if the Zn coating falls off at some places, the base metal (Fe) does not get corroded at those places. This is because the base metal acts as cathode. In corrosion process, the cathodic metal always remains unaffected.
- Galvanized articles are not used for preparing and storing food because zinc dissolves in dilute acids producing toxic zinc compounds.

**(b) Cathodic metal coating:** It is the coating of a layer of metal which is cathodic to base metal. In this type of coating, base metal should be completely covered and there should not be any pores left over it. If some part of the base metal is left uncovered, then it undergoes more intense corrosion due to formation of smaller anodic and larger cathodic area.

Example: Coating of tin or Ni metal over iron

**Tinning:** Coating a layer of tin metal on iron by hot dipping is called as tinning. The following steps are involved in the process,

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- 1) Iron sheet is passed through organic solvent to remove oil or grease present on it.
- 2) Then it is washed with dil. H<sub>2</sub>SO<sub>4</sub> to remove any rust (Oxide layer) present on the surface (pickling)
- 3) Then it is treated with a mixture of aqueous solution of ZnCl<sub>2</sub> and NH<sub>4</sub>Cl which acts as flux and then dried.
- 4) Finally it is dipped in molten tin at 230° C.
- 5) Excess tin present on iron sheet is removed by passing hot rollers and then immersed in palm oil to prevent surface oxidation of tin.

**Applications:** Tin-coated steel is used for manufacturing containers used for storing food stuffs such as jam, instant food, milk products, pickles etc.

### Note:

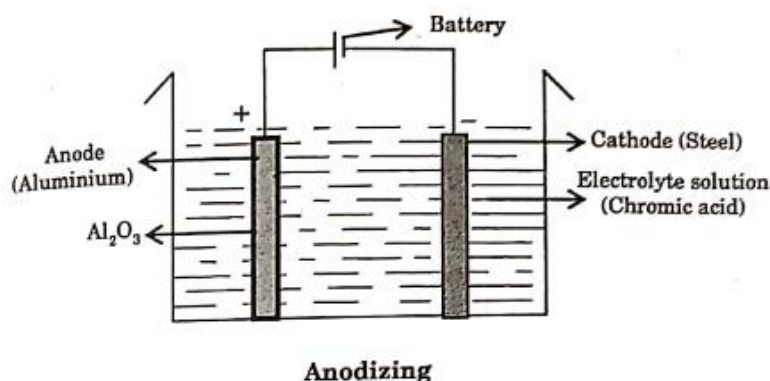
- In tin-coated iron, if a small crack is formed in the tin coating, an intense and accelerated corrosion of iron occurs at the exposed region because of the formation of a small anodic area (iron) and large cathodic area (tin).
- Copper utensils are coated with tin to prevent contamination of food with poisonous copper salts.

**(ii) Inorganic coating - Surface conversion coating:** In this method, outer surface of the base metal is converted into a protective coating through appropriate chemical modification.

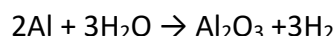
**(a) Anodizing:** It is the process of oxidation of outer layer of metal to its metal oxide by electrolysis. Oxide layer formed over the metal itself acts as protective layer.

Anodized coating is generally produced on non ferrous metals like Al, Zn, Mg and their alloys by anodic oxidation process.

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- In anodizing of aluminium, it 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 around 40°C.



- Making the article anode, voltage should be applied above 40V with lead or Steel is taken as cathode.
- A current density of 100 A/m<sup>2</sup> or more is applied which oxidizes outer layer of Al to Al<sub>2</sub>O<sub>3</sub> that gets deposited over the metal.
- Anodised surfaces show good adhesion to paint. They can also be colored to get different shades by absorbing organic or inorganic pigments on to the surface before sealing.

**Note:** On anodizing, Al<sub>2</sub>O<sub>3</sub> is formed on the surface as a porous layer. The layer may be made compact by sealing, which involves heating with boiling water or steam. During sealing, Al<sub>2</sub>O<sub>3</sub> is converted into Al<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O which occupies higher volume. Therefore, the pores are sealed.

Anodized Al is used as an attractive, highly durable, corrosion resistant material in exterior for roofs, walls, buildings, and also in many home appliances and consumer products. Also anodised aluminium is used in window frames, office partitions, tiffin carriers, etc.

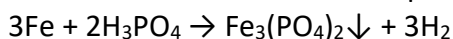
**(b) Phosphating:** Converting the surface metal atoms into their phosphates by chemical or electrochemical reactions is called phosphating.

The phosphating bath contains three essential components:

- Free phosphoric acid– It reacts with the metal surface.
- Metal phosphates of zinc and manganese– They increase adherence and decrease porosity of the coatings.
- An accelerator such as nitrites, chlorates, peroxides, etc. – They speed up the reaction.

## Unit IV Corrosion Chemistry

The process is carried out at a pH of around 3 and a temperature of 35-40°C. The reaction includes dissolution of metal as ions, forming a phosphate with the bath solution which subsequently gets a deposited on the surface of the metal. The reaction can be represented as



Phosphating not only improves the corrosion resistance but also imparts good paint adhesion quality to the surface.

Originally phosphate coating was applied only on Fe and steel. But now it has been extended, to Zn, Al and their alloys.

**Applications:** Phosphate coating is given as an under layer before painting the car bodies, refrigerators and washing machines.

**(iii) Organic coating:** Coating of metal surfaces with organic materials, particularly paints and lacquers is the most widely used anti corrosion coatings. The functions of organic coatings are of two folds:

1. 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.
2. The pigments, (red lead, zinc, chromate, etc.) or drying oils (linseed oil, wood oils, etc.) present in the paint often exert an inhibitive action by electrochemical and other means.

The requirements of a good organic coating are:

- It should adhere tenaciously to the metal surface and improve its physical appearance.
- The film formed should be continuous, uniform, and impervious to air and water.
- Should be chemically inert to the corrosion environment.
- Should have reasonably long life.
- Should have proper application methods.

The application of coating involves the following sequence: **Surface preparation, priming, filling, sanding, and finishing or top coats.** Surface preparation includes degreasing the surface, and ensuring dry and scale free surface. A high degree of protection is attained by application of several coats of paints of different compositions. The first coat is the primer, such as phosphate coating which must be strongly adhered to the surface of the articles to be subsequently painted. Fillers such as nitro cellulose, epoxides, etc., are applied on the well dried primed surface in order to improve the external appearance of the paint and to produce a smooth coating. After drying, the roughness and irregularities and the surface are smoothened by means of emery paper before applying the finishing or top coats.

Organic coatings are applied by different methods such as brushing, spraying, dipping, roller coating, etc. Break down of the organic coating may cause severe corrosion of the exposed metal parts.



## Unit IV Corrosion Chemistry

### (2) Corrosion Inhibitors:

Corrosion inhibitors are chemical substances which are added in small quantities to the corrosive environment to decrease the rate of corrosion. Inhibitors slow down the anodic reaction or the cathodic reaction generally by forming a protective film on the anodic region or the cathodic region.

There are two types of corrosion inhibitors namely anodic corrosion inhibitors and cathodic corrosion inhibitors.

#### (i) Anodic inhibitors:

- Anodic Inhibitors: If the formation of  $M^{n+}$  is prevented, the cathodic reaction also stops and thereby the corrosion process is retarded.
- This is achieved by the addition of anions such as chromate, tungstate, molybdate, phosphate etc.

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 covered with the protective film leaving the remaining anodic region exposed to the environment. Formation of small anodic area results in intense corrosion.

#### (ii) Cathodic inhibitors:

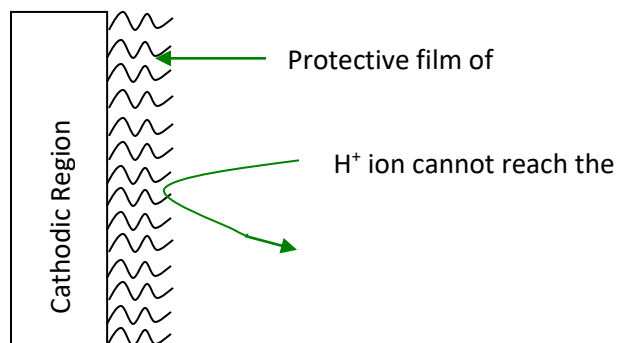
The two important types of cathodic reactions are liberation of hydrogen or absorption of oxygen. Therefore, there are two distinct approaches in achieving inhibition of cathodic reactions.

- a) by preventing the liberation of hydrogen or
- b) by preventing the absorption of oxygen.

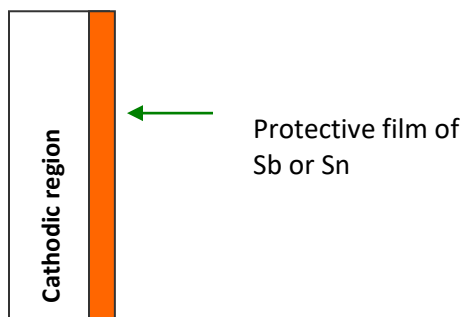
a) **Inhibition of hydrogen liberation:** The liberation of hydrogen at cathode can be prevented either by preventing the diffusion of  $H^+$  ions to the cathode or by increasing the hydrogen over voltage on the metal surface.

The diffusion of  $H^+$  ions to the cathode is prevented by the addition of certain organic compounds which contain nitrogen or sulphur. Aliphatic amines, urea, thiourea, mercaptans, heterocyclic compounds are widely used as cathodic inhibitors. Such substances, when added to the corrosion medium, are adsorbed on the cathodic region forming a protective film, preventing the  $H^+$  ions from coming in contact with the cathodic metal surface.

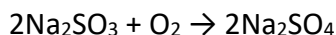
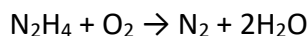
## Unit IV Corrosion Chemistry



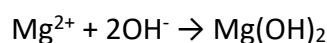
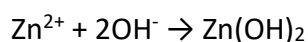
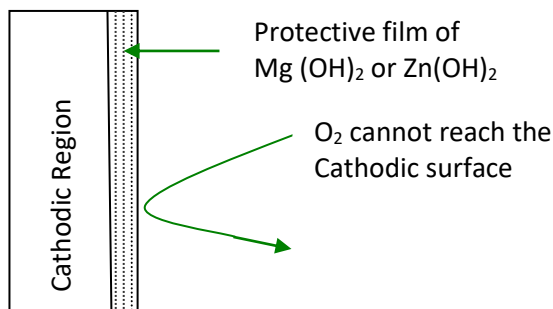
The evolution of hydrogen at the cathode can also be prevented by increasing the hydrogen over voltage. This is achieved by the addition of oxides of arsenic, antimony or salts like sodium meta-arsenite. They deposit as adherent metallic film on the cathode region and thereby prevent the liberation of hydrogen, as the hydrogen over voltage on these metals is very high.



- b) **Inhibition of oxygen absorption:** The absorption of oxygen can be stifled either by removing the oxygen from the corrosive media or by simply decreasing the diffusion rate of oxygen to cathode. The first objective is achieved by adding reducing agents or oxygen scavengers such as hydrazine, sodium sulfite etc., into the corrosion medium. These substances remove oxygen from the corroding environment by reducing it.



The second objective is achieved by adding salts such as  $\text{ZnSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{NiSO}_4$  etc. into the corrosion medium. The cations of the salts ( $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ ) migrate towards the cathode surface and react with the hydroxyl ions formed at the cathode, to deposit their hydroxides on the cathodic sites.



The protective film being impermeable to oxygen prevents its diffusion to the cathodic region. The action of an inhibitor depends on the nature of the metal to be protected as well as corrosive environment. It is, therefore, necessary to choose an appropriate for a particular system.

## 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.
- Generally lose their effectiveness rapidly as the concentration and temperature of the environment increase.

## (3) Cathodic protection:

Cathodic protection is a method of protecting a metal or alloy from corrosion by converting it completely into cathodic and no part of it is allowed to act as anode.

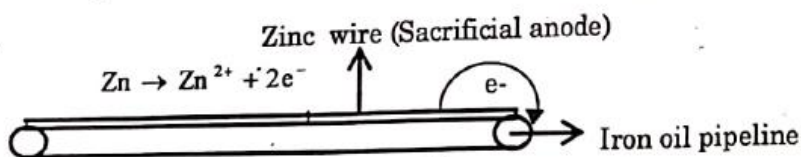
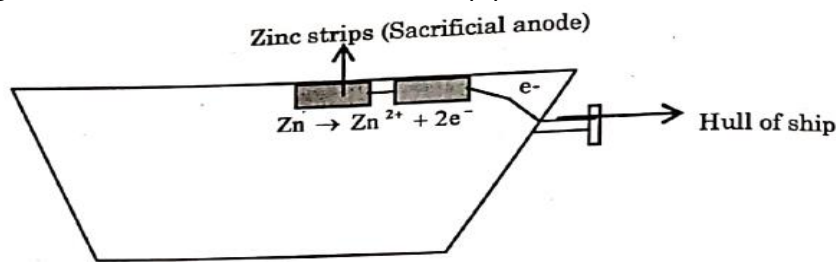
### (i) Sacrificial anode method:

- In this method, protected metal structure is converted into a cathode by connecting it to a more active metal.
- This active metal acts (example: zinc, magnesium, aluminium) 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.

## Example:

- A magnesium block connected to a buried oil storage tank
- Mg/Zn bars are fixed to the sides of ocean going ships to act as sacrificial anodes
- Mg/Zn blocks are connected to buried pipe lines



## Advantages:

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

## Disadvantages:

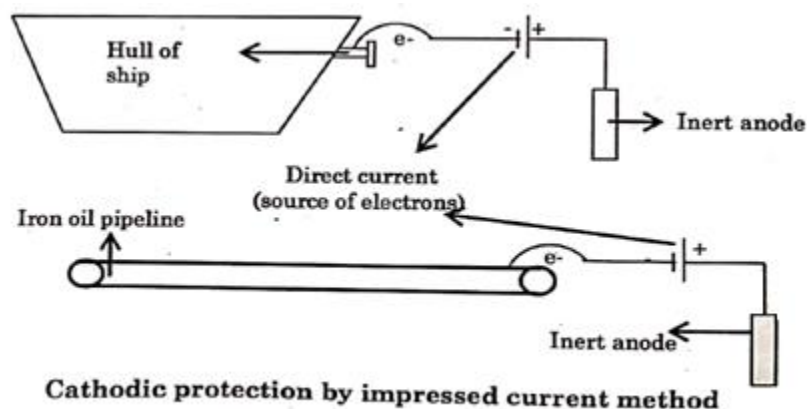
- Involves recurring expenditure for replacement of consumed anodes.

## (ii) Impressed current method:

- Another method of providing cathodic protection is by applying a direct current larger than the corrosion current.
- The protected metal is made cathodic by connecting it to the cathode of the external source of current.
- The metal structure being cathode does not undergo corrosion.

## Unit IV Corrosion Chemistry

- Anode being inert remains unaffected.
- Graphite is widely used as the inert anode in this method. Platinum, silicon, iron are also used as anodes.



### Advantages:

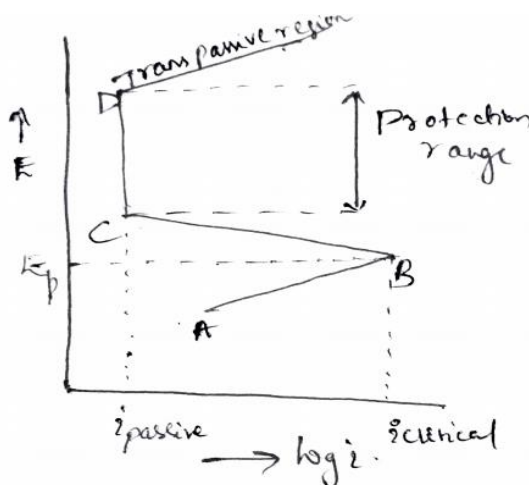
- One installation can protect large area of metal
- Low maintenance cost

### Limitations:

- Rather expensive, since it needs high current for safe protection of structure.
- If hydrogen liberation is the cathodic reaction on the metal surface, then the protected metal may suffer by hydrogen embrittlement.
- If the impressed current is not uniform on the entire surface of the protected structure, localized corrosion takes place on the protected metal.

### (4) Anodic protection:

The prevention of corrosion by the impressed anodic current is called as anodic protection. The active – passive transition of the metals (nickel, iron, chromium, titanium and their alloys) with the application of the potential can be explained from potential-current curve as shown in the figure.

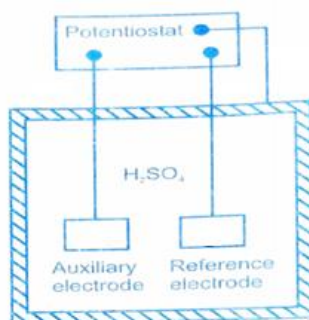


- The curve is obtained by applying a known potential to the metal specimen and measuring the current changes.
- As the potential is increased, initially the current also increases (AB), and it indicates the dissolution of metal.
- This trend continues until the current reaches a critical value ( $i_{crit}$ ) 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 ( $E_p$ ).
- Above  $E_p$ , the current flow decreases and reaches a minimum value called passivation current,  $i_{passive}$ .
- Passive region – If the potential is increased further, the metal remains unattacked up to a particular potential is reached (CD). In this range, corrosion rate of the metal is very small. This potential range, in which anodic potential can be achieved, is called protection range or passive region.
- The anodic protection to a structure is applied by using a device called potentiostat.

## 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 storage tank, another to an auxiliary cathode (Pt) and the third connected to a reference electrode.



- It maintains a constant potential between tank and the reference electrode, corresponding to the passive range.
- Anodic protection can be successfully used to improve corrosion resistance of metals or alloys, provided the following conditions are fulfilled.
- The metal or alloy must be capable of becoming passive on the application of anodic current in the region to which it is exposed.
- It must require a small current to maintain passive state-high corrosion resistance at low energy consumption.
- A sufficiently broad potential range in which the metal or alloy is stably passive.

The primary advantages of anodic protection are its applicability in extremely corrosive environments and its low current demand. However, the anodic protection has the following **limitations**:

- Anodic protection is restricted to the metal that show active-passive behaviour.
- Its initial installation cost is high.
- It can reduce corrosion rate to zero unlike cathodic protection.

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1. [https://www.fabory.com/knowledge\\_center/technical/surface\\_treatments](https://www.fabory.com/knowledge_center/technical/surface_treatments)
2. Gadag, R.V. and NityanandaShetty A., I.K. International Publishing House, Third edition reprint, 2015.