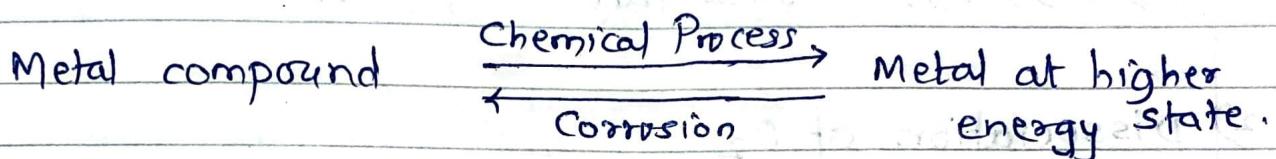


## CORROSION AND ITS PREVENTION

Corrosion : Destruction of a metal by chemical or electrochemical attack of environment, starting at its surface, is known as corrosion.



### Types of corrosion

- 1) Dry | Atmospheric | Direct Chemical corrosion (corroding medium = gases)
- 2) Wet | Electrochemical | Immersed Corrosion (corroding medium = aqueous)

#### 1) Dry | Atmospheric | Direct Chemical Corrosion

- Due to direct attack of atmospheric gases like  $O_2$ ,  $CO_2$ ,  $SO_2$ ,  $H_2S$ ,  $H_2O$ ,  $NH_3$ ,  $Cl_2$ ,  $NO_2$  etc.
- Rate of corrosion depends upon
  - ① Temperature
  - ② Chemical Affinity between metal & gas
  - ③ Nature of oxide film on surface of metal,
  - ④ Moisture in air.

① Temperature : Higher is temp., faster is the rate of corrosion.

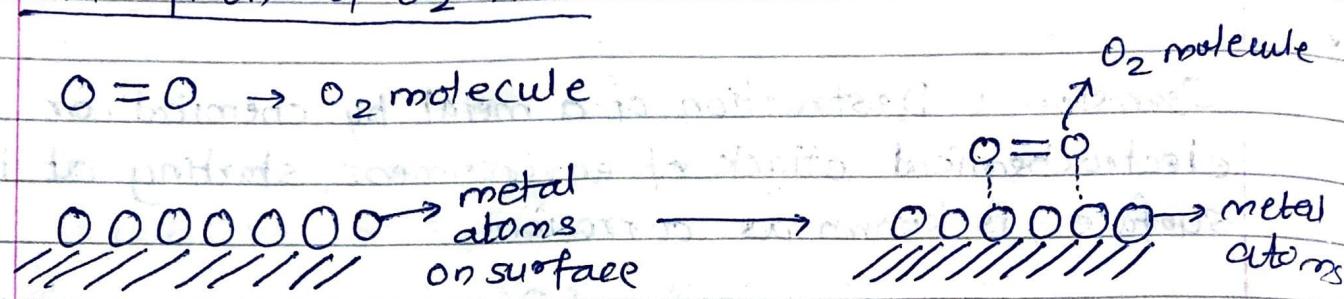
② Chemical Affinity between metal & gas

If metal is placed higher in Galvanic Series, then it is chemically active & gets corroded faster.

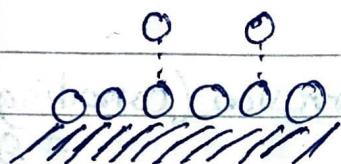
Gases like  $O_2$  &  $CO_2$  are less reactive,  $H_2S$  is more reactive.

## Mechanism of Corrosion between Iron & Oxygen

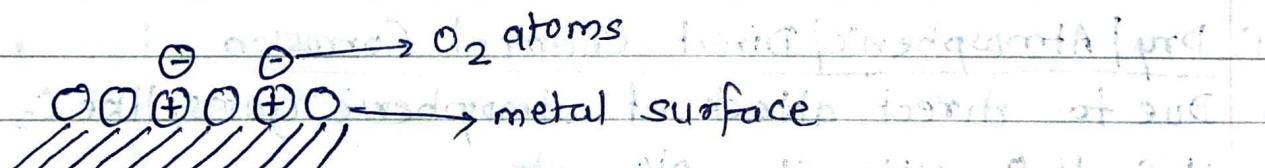
### 1) Adsorption of $O_2$ metal



### 2) Dissociation of $O_2$



### 3) Loss of $e^-$ by metal atom



### 4) Formation of metal oxide



### ③ Nature of oxide film

- i) Porous film - If the oxide film is porous,  $O_2$  gas molecules penetrate & continue corrosion of underlying metal until the whole metal gets destructed.  
e.g. Iron

- ii) Non-porous film :- When the oxide film is non-porous, then further corrosion stops. e.g. Chromium, tin
- iii) Unstable oxide film - When the oxide film formed is unstable & it decomposes back into metal & oxygen then there is no corrosion takes place. e.g. Gold, Platinum
- iv) Volatile oxide film - If metal oxide film is volatile, then its evaporation takes place & underlying fresh metal is exposed to further attack of  $O_2$ . e.g. Mb-oxide film

### Pilling-Bedworth Rule -

It gives idea about nature of oxide film whether it is porous/non-porous

$$\text{Pilling-Bedworth Ratio (PBR)} = \frac{\text{Volume of metal oxide}}{\text{volume of metal consumed}}$$

- If volume of oxide is smaller than the volume of metal consumed in metal oxide formation, then the film is porous & if metal oxide formed has greater volume than the metal consumed, then film is non-porous.

If  $PBR = 1 - 1.45$ , then film is Non-porous

$PBR < 1$ , then Porous.

### 2) Wet Electrochemical Corrosion

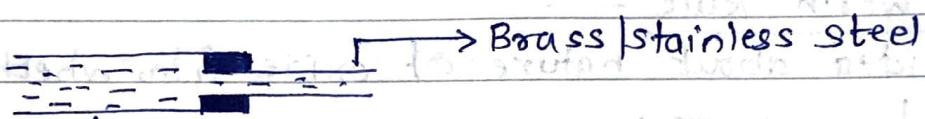
Corrosion of a metal by aqueous conducting medium, with formation of anodic & cathodic areas, is known as wet/electrochemical/immersed corrosion.

Wet corrosion is of 2 types

- a) Galvanic corrosion
- b) Concentration cell corrosion

(i) Galvanic Corrosion: Electrochemical corrosion of a metal by attack of an aqueous conducting medium, with formation of galvanic cell, is known as galvanic corrosion. The galvanic cells are formed in following cases:

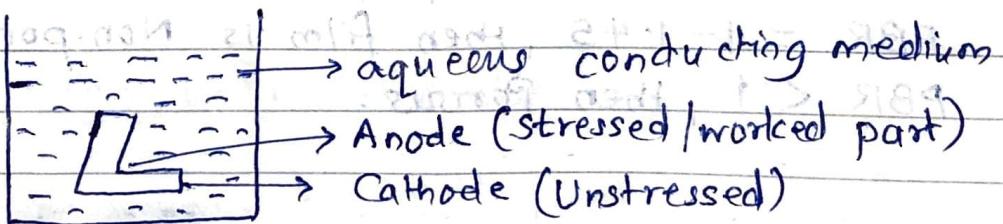
(i) Two dissimilar metals in contact: When two dissimilar metals are in contact with each other & there is aqueous conducting medium in their contact, galvanic cell is formed. e.g. Tap of brass/stainless steel



→ Galvanised pipe (gets corroded as higher placed in G.S.)

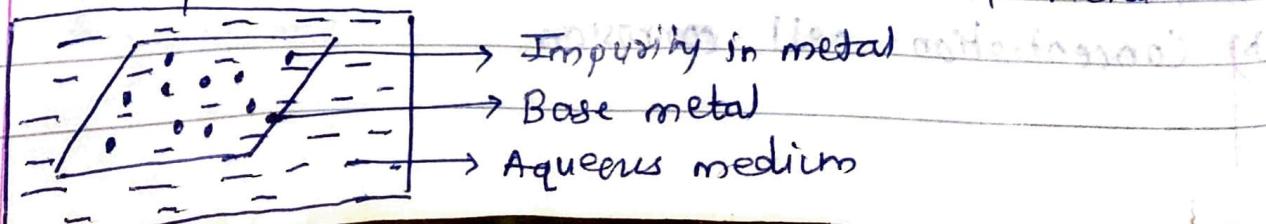
(ii) Stressed & unstressed parts on the same metal:

Worked/stressed part of metal acts as anode & gets corroded in aqueous conducting medium. Unstressed part acts as cathode. e.g. Bent part of a plate



(iii) Impurities in metal: A large no. of tiny galvanic cells are formed on the surface of impure metal.

Impurity may act as anode if it is higher placed in G.S. (Galvanic series). If impurity acts as anode, small pits are formed on the surface of metal.

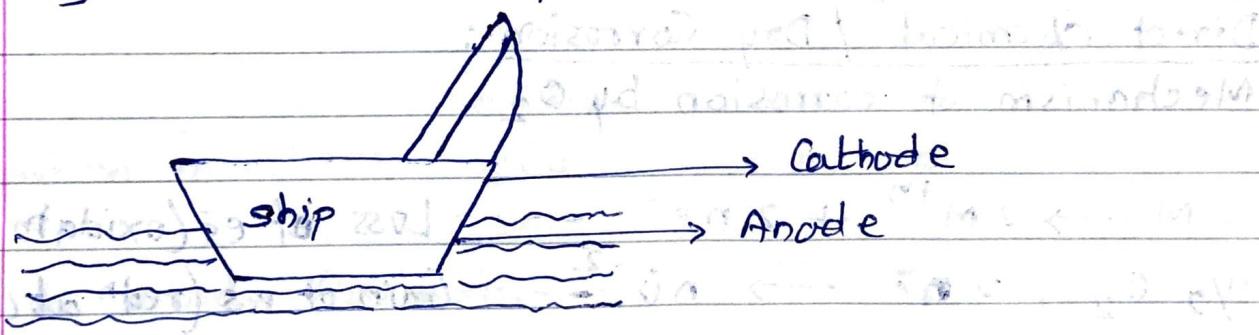


b) Concentration cell corrosion (Differential Aeration Cell)  
Corrosion)

- Whenever a part of the metal is in contact with higher concentration electrolyte or  $O_2$  than the remaining part, there is formation of concentration cell.
- The part of metal in contact with lesser  $O_2$  or lower electrolyte concentration, acts as anode & gets corroded. Remaining part acts as cathode.
- The concentration cells formed due to varying  $O_2$  conc. in a metal, are called as differential aeration cells.
- These are formed in 4 situations:

(i) Partial Immersion of a metal in electrolyte:

Immersed part of metal is poorly oxygenated  $\therefore$  acts as anode & gets corroded. Metal part which is exposed to higher conc. of  $O_2$  (air) acts as cathode.



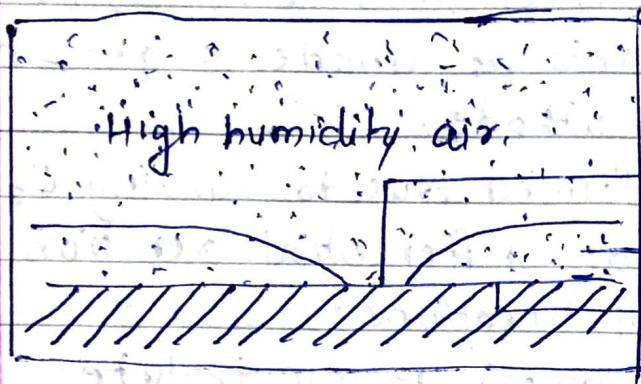
(ii) Partial Burial in ground:

A metal partially buried in ground (poles) have aerial part more oxygenated (cathode) & metal in contact of moist soil poor oxygenated (anode)

(iii) Crevices: When two plates of same metal are not fitted properly, there is small gap between them. The metallic surface in gap which is poorly oxygenated acts as anode & gets corroded.

(iv) Oxide film on metal surface partially ruptured

If the non-porous oxide film on metal gets ruptured partially, then the open part is more oxygenated & the covered part is poorly oxygenated (anode & corrodes)

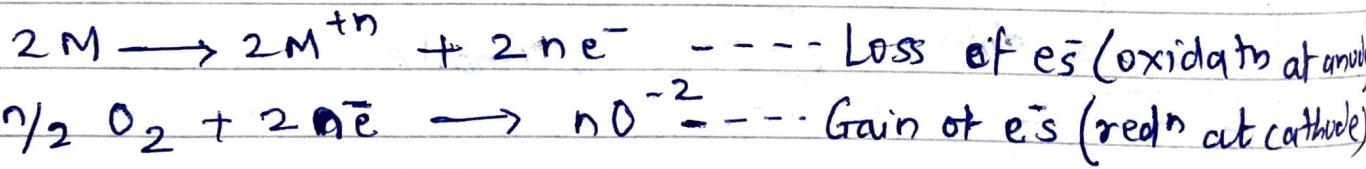


→ Cathode (highly oxygenated)  
→ Oxide film  
→ Anode (poorly oxygenated)

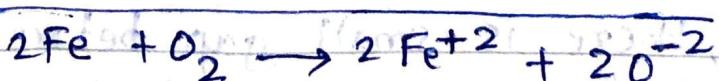
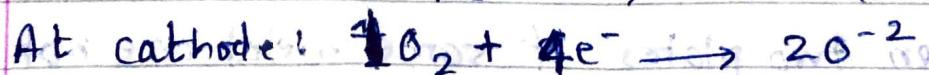
### Mechanism of corrosion

#### 1) Direct Chemical / Dry Corrosion:

Mechanism of corrosion by  $O_2$

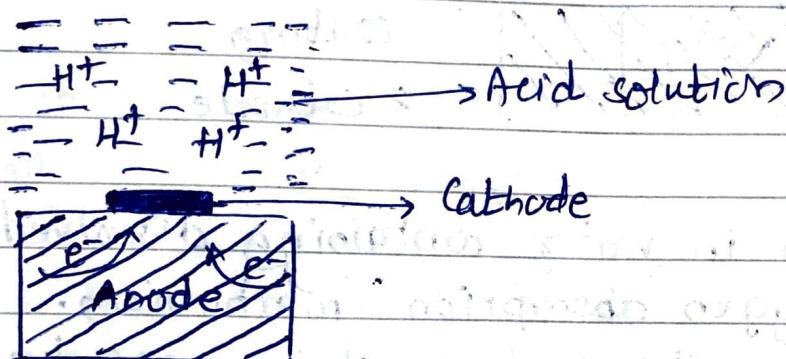


#### Mechanism of corrosion betw $O_2$ & Iron



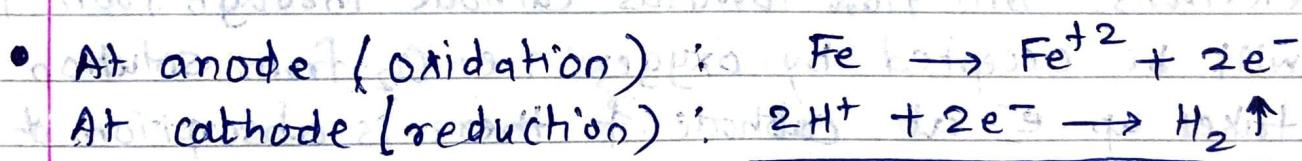
- 2) Electrochemical / wet corrosion
- a) Galvanic cell formation corrosion mechanism  
It takes place by 2 ways
- Hydrogen evolution mechanism
  - Oxygen absorption mechanism
- b) Concentration cell corrosion mechanism

(i) Hydrogen Evolution Mechanism



Large area: anode  
Small area: Cathode

- Hydrogen evolution type of corrosion of metals occurs when metals <sup>are</sup> exposed to acidic environment.

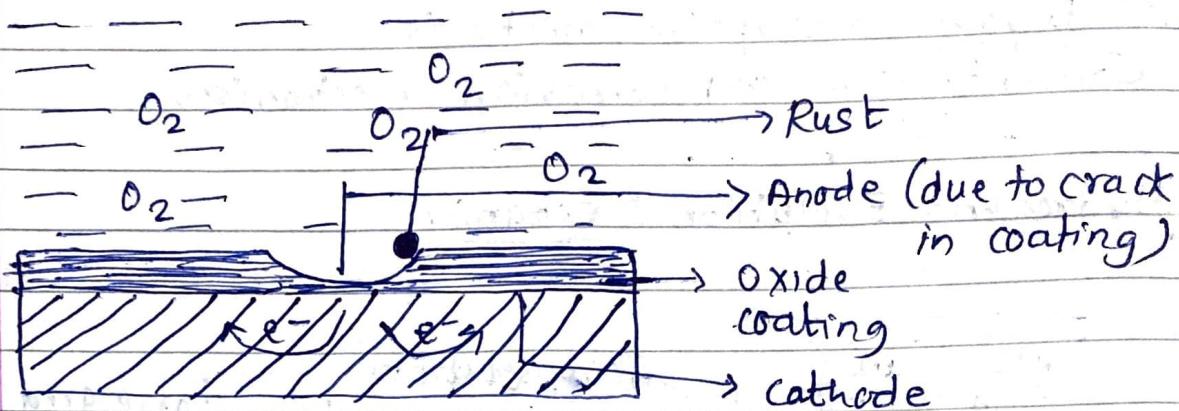


- Electrons flow towards cathode. Iron passes into solution as  $\text{Fe}^{2+}$ . Hydrogen from acid accepts  $e^-$ . evolution of hydrogen gas takes place at cathode.
- Product of corrosion: Metal will get dissolved in acid solution with evolution of hydrogen gas.

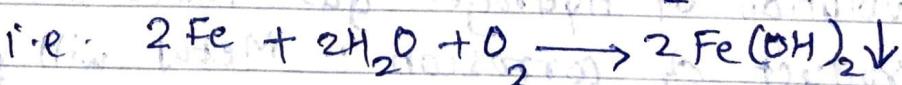
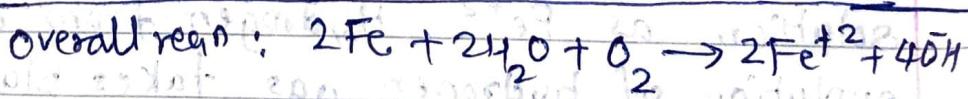
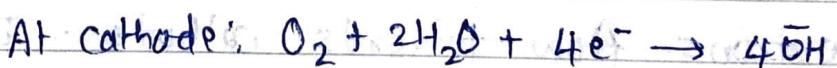
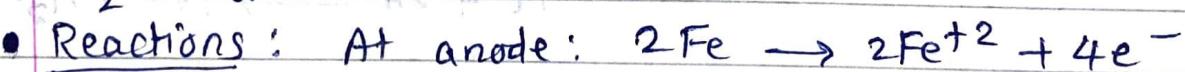


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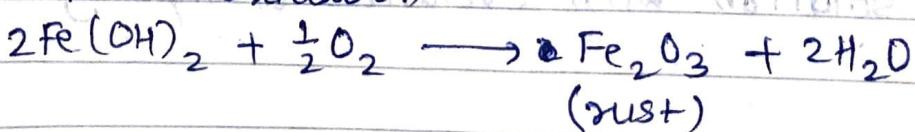
### (ii) Oxygen absorption mechanism



- Rusting of iron in water containing dissolved oxygen occurs by oxygen absorption mechanism.
- Anode areas on the surface of iron are due to presence of cracks in metal coating & cathodic area will be surface of coated metal.
- At anode, iron will dissolve by oxidation. Then electrons will flow towards cathode through iron & will be accepted by oxygen i.e. O<sub>2</sub> from solution, takes up e<sup>-</sup> at cathode & there is absorption of O<sub>2</sub> at anode.



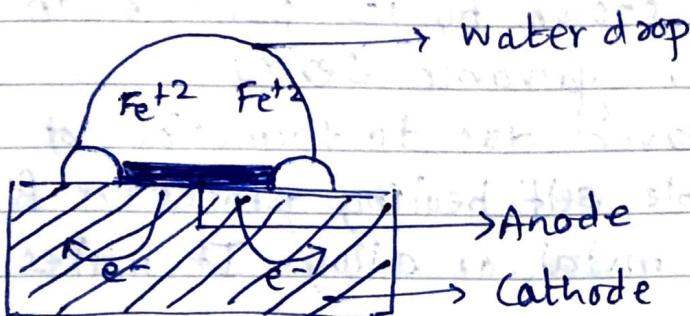
- On further oxidation



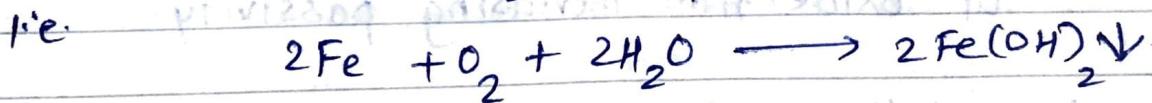
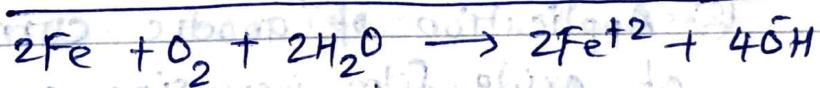
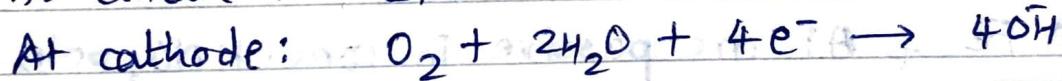
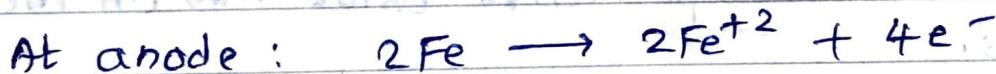
Product of corrosion - Fe<sub>2</sub>O<sub>3</sub> (rust)

- If electrolyte NaCl is used, then product is Fe(OH)<sub>3</sub> ↓

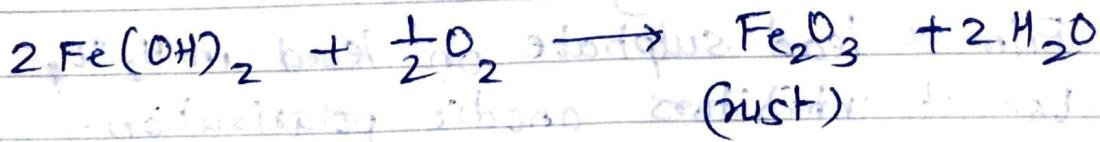
### b) Concentration cell corrosion mechanism



- Cathode: Highly oxygenated part
- Anode: Poorly oxygenated part  
when water droplet is on the surface of metal, this type of corrosion takes place.



On further oxidation



## Factors affecting corrosion

Rate & extent of corrosion depends upon

A) Nature of metal      B) Nature of environment

### A) Nature of metal

#### 1) Position of metal in galvanic series (G.S.):

- In a cell, higher placed metal in G.S. acts as anode & gets corroded.
- The rate & severity of corrosion depends upon their difference in positions. More the metals apart in G.S., faster is the corrosion of anode & more is the current generated.

#### 2) Relative areas of anode & cathode:

- If cathode to anode area ratio is greater, rate of corrosion is faster.
- A better design of cell is one, in which anode is larger than cathode i.e. metal higher placed in G.S. is used in larger proportion than the metal placed lower placed in G.S.

#### 3) Purity of metal:

- Impurities in metal form large no. of minute galvanic cells in presence of conducting medium.
- If impurity is lower placed in G.S., then metal corrodes & if impurity is higher placed in G.S., impurity corrodes with formation of pits on metal.

#### 4) Physical state of metal:

- Smaller the grain size of metal / alloy, greater is the rate of corrosion. e.g. Steels get corroded easily than cast iron because grains in steels are of smaller size.
- Areas under stress in same metal act as anode.

5) Nature of oxide film:

- If the oxide film formed is protective, non-porous, corrosion does not take place.
- If film is porous, metal continues until its complete destruction.

6) Oxide film:

- If the metal is higher placed in EMF series than hydrogen, liberates Hydrogen in acid solution.
- Due to this Hydrogen bubbles, the contact between metal & acid solution is lost & this leads to decreasing rate of corrosion i.e. such metal develops corrosion resistance to some extent or the metal behaves as if it is placed lower than its actual position in EMF series.
- To restore position of metal, extra voltage is necessary. This extra voltage is known as 'Overvoltage' e.g. Zn, Pb, Ni.

B) Nature of Environment

1) Temperature:

- Rate of dry corrosion is faster at higher temp. because gases are activated.
- Rate of wet corrosion increases with increase in temperature.

2) Moisture:

- Rate of dry corrosion increases in presence of moisture.
- In presence of moisture, galvanic & differential aeration cells are formed & rate of corrosion is fast.

3) pH :

- Acidic media have more corrosive effects on metals. Because  $e^-$  liberated from anode are consumed by  $H^+$  from acid solution.
- Amphoteric metals i.e. Al, Pb are more attacked by alkaline media
- Pourbaix diagram gives clear idea about the optimum pH for minimum corrosion of metal.

4) Conductivity of corroding medium

- Higher the electrical conductivity of soil, water or aqueous corroding medium, higher is the rate of electrochemical corrosion.

5) Nature of ions in medium

- $Cl^-$ ,  $NO_3^{2-}$  ions have ability to break & non-porous oxide films of metals & increases corrosion.
- The presence of oxalate ions,  $PO_4^{2-}$  ion, silicate ion have ability to slow down rate of wet corrosion.

## Difference between EMF & Galvanic Series

### EMF series

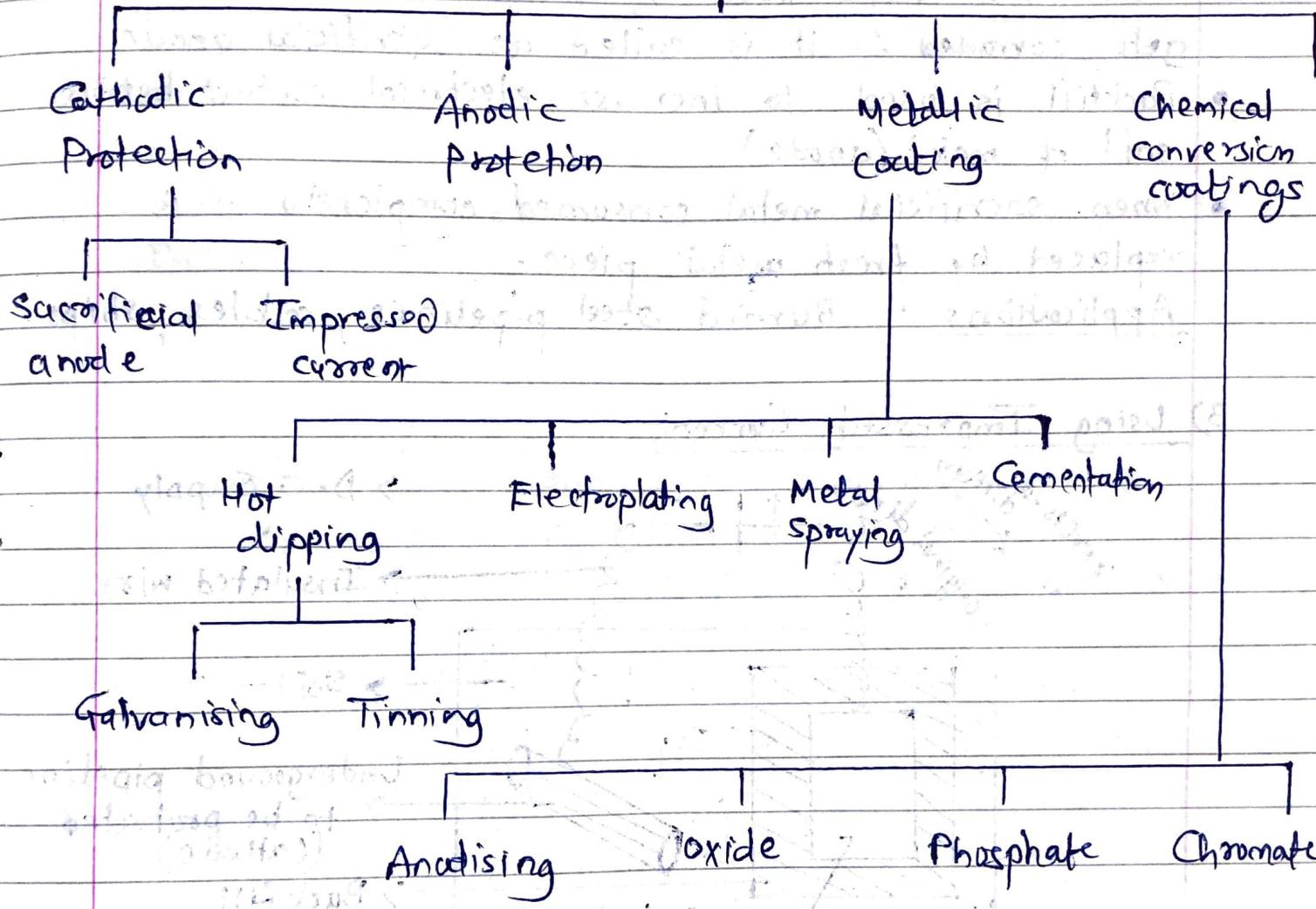
- 1) Pure metal free from oxide film on surface, is taken for finding electrode potential.
- 2) The electrolyte solution in contact of metal surfaces electrode is 1 Molar.
- 3) No any alloy finds its position in EMF series.
- 4) Some non-metallic electrode system also find their position in emf series.
- 5) Position of a metal is fixed and definite values of electrode potentials are given. EMF values given for the metal electrodes.
- 6) EMF series predicts the theoretical voltages of cells and the relative displacement tendencies.

### Galvanic Series

- 1) Metal/alloy in its practically used form along with oxide film on surface is taken for electrode potential.
- 2) The sea water is the electrolyte medium in contact with the metal or alloys.
- 3) Various alloys find their position in galvanic series.
- 4) No any nonmetallic electrode system present.
- 5) Position of metal or alloy may shift with the entry of newly discovered alloy, values of electrode potentials not given necessarily.
- 6) Galvanic series predict relative corrosion tendencies of metal & alloys.

## Methods of Corrosion Control

### Corrosion Control Methods

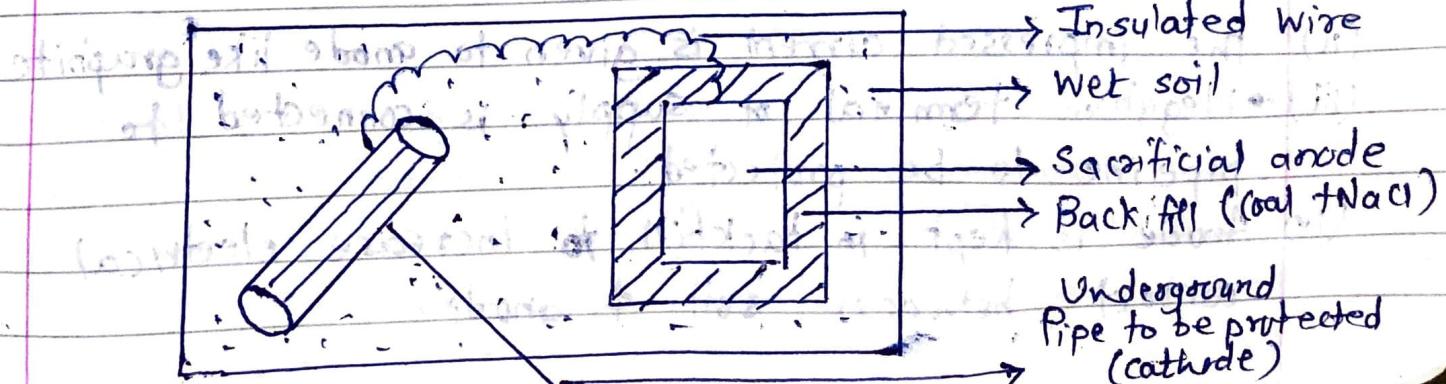


#### I) Cathodic Protection

Principle : The metal to be protected is forced to behave as cathode

There are two ways to do so

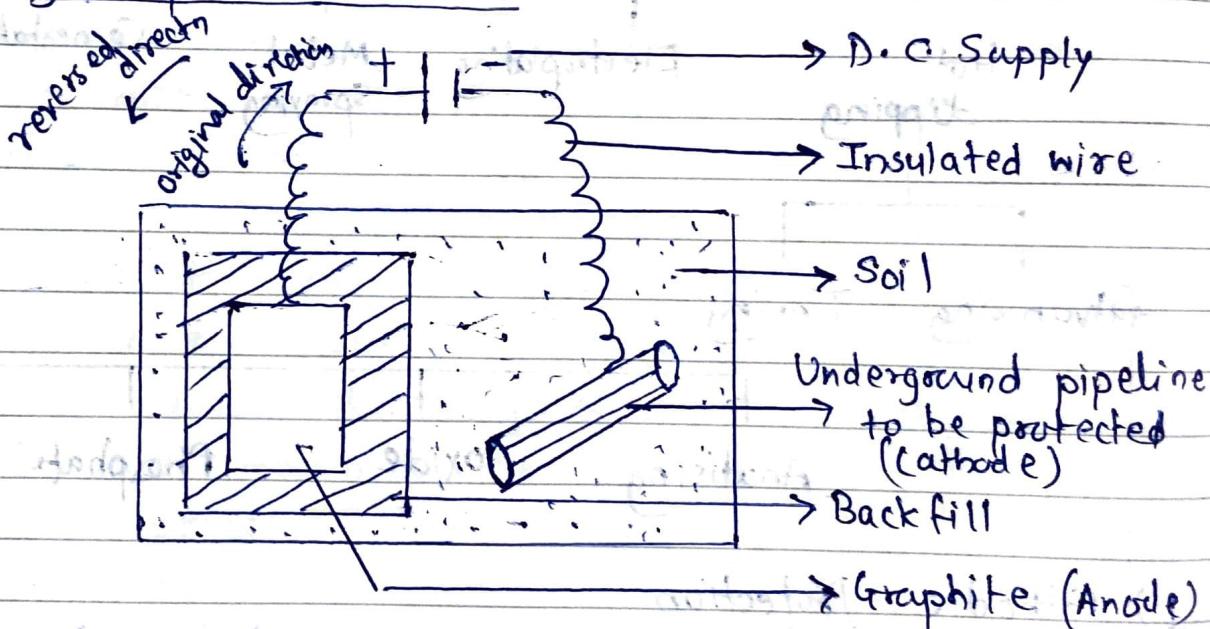
##### A) Using) Sacrificial Anodes



Method:

- The metal to be protected is connected to anodic metal by a wire.
- More active metal like Zn, Al, Mg acts as anode & gets corroded ∵ it is called as sacrificial anode.
- Backfill is used to increase electrical contact between soil & metal (anode)
- When sacrificial metal consumed completely, it is replaced by fresh metal piece.

Applications: Buried steel pipelines, cables, ships.

B) Using Impressed CurrentMethod

- Impressed current is applied in opposite direction to nullify the corrosion current & convert corroding metal from anode to cathode.
- The impressed current is given to anode like graphite
- Negative terminal of supply is connected to pipeline to be protected.
- Anode is kept in backfill to increase electrical contact between soil & anode.

## Applications

Used in (i) Open water box coolers

(ii) Water tanks (iii) Buried pipelines

(iv) Condensers (v) Transmission line towers.

This method is suited to large structures & long term applications.

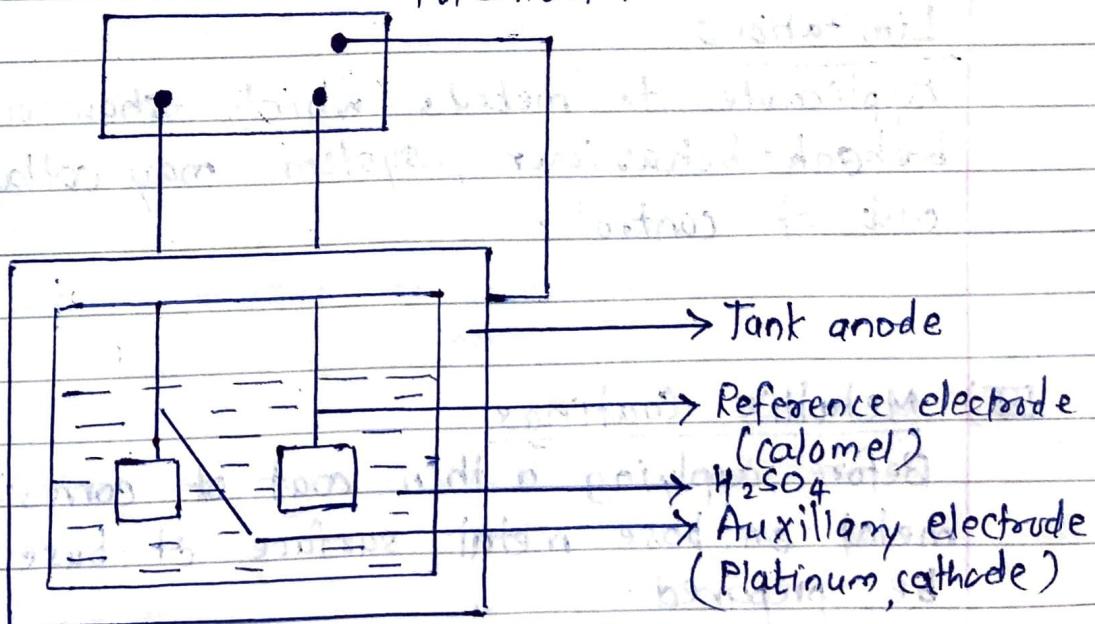
## Limitations

- (i) High costs
- (ii) Stray currents, corrode nearby pipelines.
- (iii) Protection should not lead to over-protection.

## II) Anodic Protection

Principle: A metal/alloy having wider range of passivity voltage, is made anodic & voltage in passivity range, is applied over it to control its corrosion by strongly corroding media.

Potentiostat



- (i) Metal to be protected is made anode & that anode is made passive i.e. by forming protective film on it using externally applied currents.
- (ii) To protect the metal making it anode, potentiostat

is used. Potentiostat maintains metal at constant potential with respect to reference electrode. Out of 3 terminals of potentiostat, one is connected to the metal to be protected, second to auxiliary electrode, third to reference electrode.

- (iii) The minimum/negligible current indicates that anodic protection is taking place successfully.
- (iv) If corrosion current is high, system goes out of control & electrical connections should be removed immediately.

### Applications

Chemical reactors, Industrial water coolers, metal condensers, Pipeline carrying corrosive liquids.

### Advantages

Low cost, applicable to high corrosive media, Reliable, Protection current gives idea about corrosion rate.

### Limitations

Applicable to metals which show active-passive behaviour, system may collapse if goes out of control.

## III) Metallic Coatings

Before applying a thin coat of corrosion resistant metal on base metal, surface of base metal should be prepared.

To prepare base metal for coating

- 1) Solvent cleaning - to remove oily matter using organic solvents
- 2) Alkali cleaning - to remove old paint coatings, must use alkali solution ( $\text{Na}_3\text{PO}_4$ )

3) Mechanical cleaning - to remove rust by using brush, scrapers.

4) Flame cleaning - to remove scale, moisture.

5) Sand blasting - to remove oxide scales.

Metallic coatings are of 2 types

(1) Anodic coatings (2) Cathodic coatings

(1) Anodic coatings: (i) If the coating metal is higher placed in G.S. than base metal, then coating is anodic coating. e.g. Zn, Al on steel.

(ii) If galvanic cell is formed in metal in conducting medium in conducting medium, coating metal becomes anode, & gets corroded while base metal remains protected. ∴ Anodic coatings are preferred. If anodic coating ruptures, base metal does not corrode.

(2) Cathodic coatings: (i) If coating metal is lower placed in G.S. than base metal, then coating is cathodic coatings (e.g. coating of tin on steel, silver on brass etc.). (ii) If cathodic coating is ruptured, base metal acts as anode & gets corroded in galvanic cell.

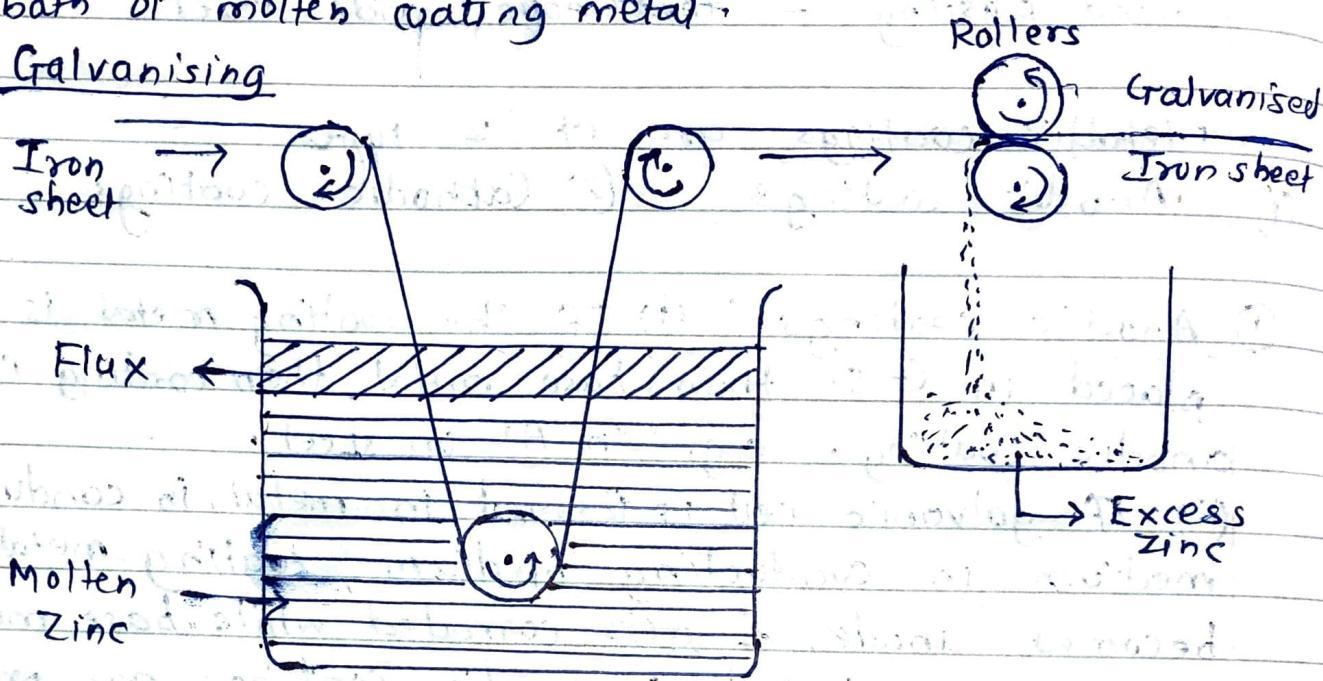
Methods of applying metallic coatings

- A) Hot Dipping
- B) Metal Spraying
- C) Electroplating
- D) Cementation

### (A) Hot Dipping

- (i) Coating of low melting metal like Zn, Sn on metals like steel, copper. (ii) Base metal is immersed in a bath of molten coating metal.

### a) Galvanising

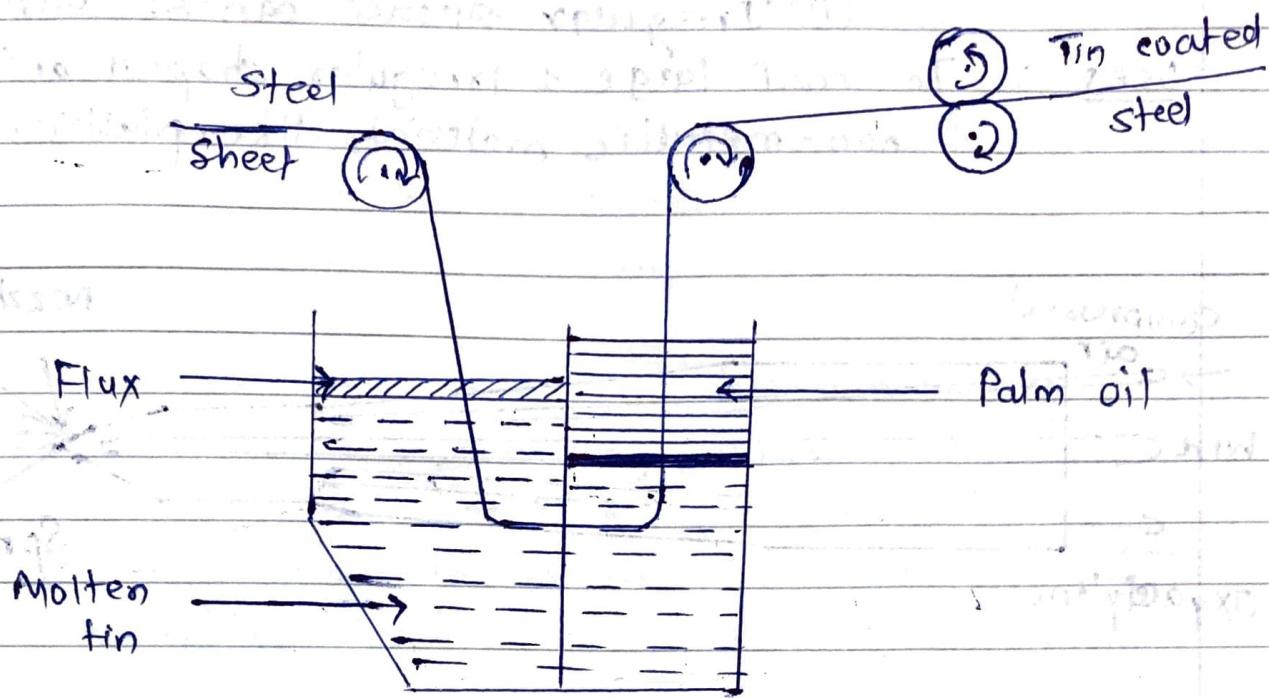


Coating of Zn on Iron/steel is called as Galvanising.

Article is cleaned with  $H_2SO_4$  & dipped in a bath of molten zinc ( $425 - 450^\circ C$ ). Surface of bath is covered with flux ( $NH_4Cl$ ). Flux prevents oxidation of molten coating metal. Then the article is rolled to make the coating of uniform thickness & then cooled.

Uses: Protection of Iron, Galvanised Iron articles are useful. e.g. wires, pipes, buckets, nails, screws. But can not be used for storing food as zinc will act to produce poisonous products.

### b) Tinning



Coating of tin on steels, known as tinning. Clean article passes through molten bath of tin ( $240^{\circ}\text{C}$ ) & then through palm oil. Palm oil protects tin-coated surface against corrosion. Rollers remove excess tin & makes uniform coatings.

Use of tinning : ① Sn has greater corrosion resistance & better glaze ② Can store foods, oil etc. ③ Cu wires, before insulation are tinned to avoid attack of sulphur from rubber.

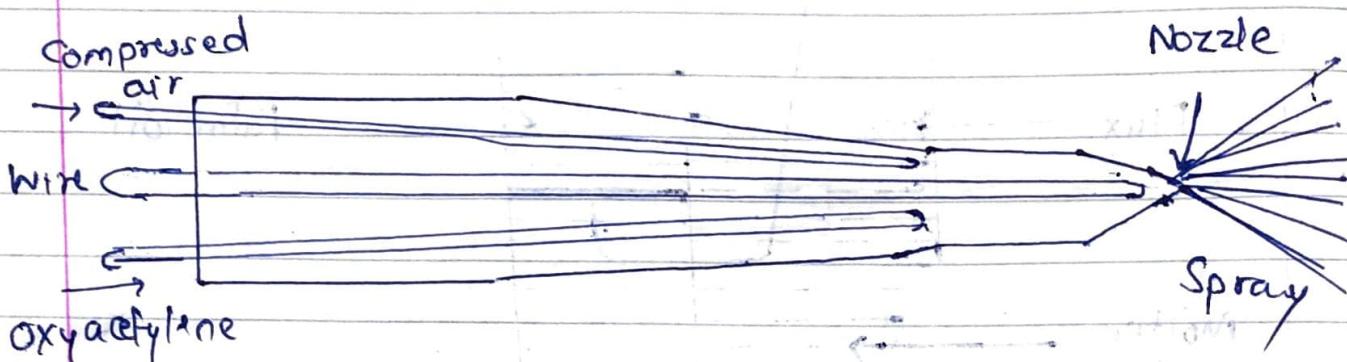
### (B) Metal Spraying

Method : ① A coating metal in molten state is sprayed on base metal. There is a spraying gun for this purpose. ② Spraying gun consists of duct for oxyacetylene gas & a provision for compressed air. ③ Coating metal is fed to gun in form of

wire & comes out as a spray which is directed on clean metal surface.

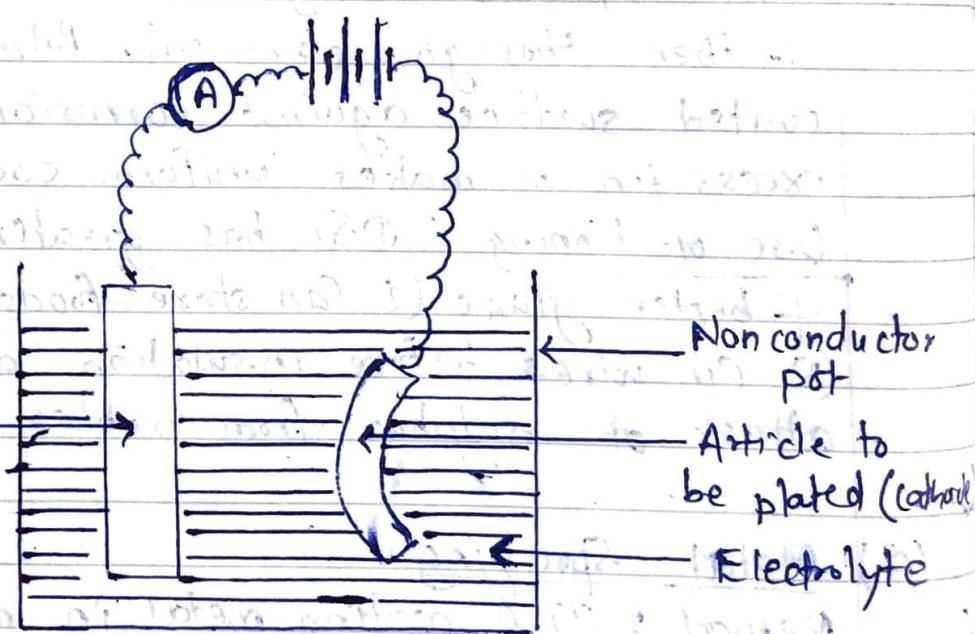
Advantages : (i) Greater speed of work working  
(ii) Irregular surface can be coated.

Uses : To coat large & irregular shaped articles & non-metallic materials like plastic.



### (C) Electroplating

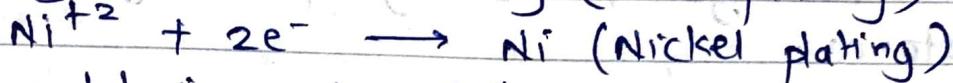
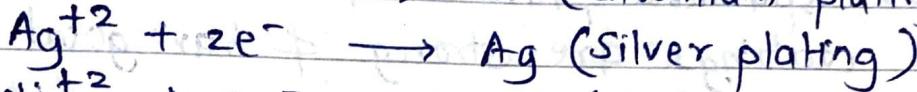
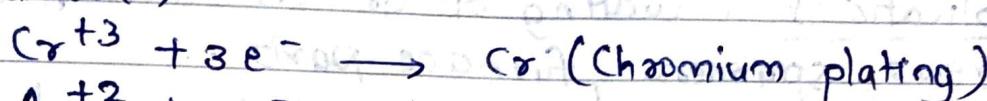
Coating metal  
(Anode)



RK

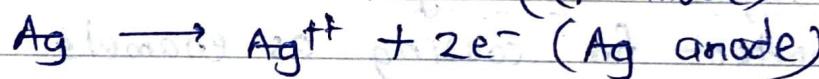
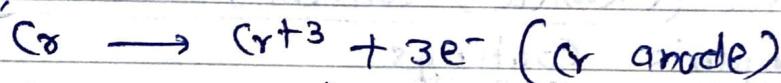
- In this, coating metal is coated on base metal on the basis of electrolysis principles.
- Method
- ① Article to be plated is cleaned.
- ② Tank contains salt of coating metal.
- ③ Article is connected to negative terminal of D.C. supply, to make it cathode. Anode is coating metal.
- ④ After suitable pH & current density, electroplating starts.

At cathode,



- The metal ions in solution migrate toward cathode article & capture electrons & forms metal atoms.

At anode,



Coating metal passes in solution as its ions.

- Metal ions discharged / accumulated on article (equal) = quantity of anode metal atoms passed in soln.
- Decrease in weight of anode = increase in weight of cathode.

### Advantages

Corrosion protection, decoration, to have attractive look, to make plastic, glass conducting.

- Coating metals  $\rightarrow$  Cu, Ni, Cr, Au, Ag, Pt
- Base metals  $\rightarrow$  Fe, steel, plastic, wood, glass.

## (D) Cementation

### Method

- Base metal articles are packed in powder of coating metal & heated to a temperature just below its melting point.
- This process is called as sherardizing if coating metal is zinc, as colorizing if coating metal is Al & chromizing if coating metal is Cr.
- Applications: Coating of articles like nuts, bolts, screws, spanners, furnace parts.
- These coatings are strong & have good abrasion resistance.

## IV) Surface (chemical) conversion Coatings / Inorganic Coatings

- Important for coating as enamels.

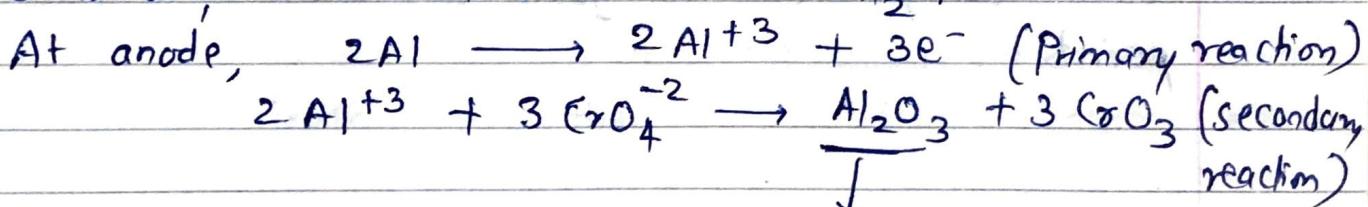
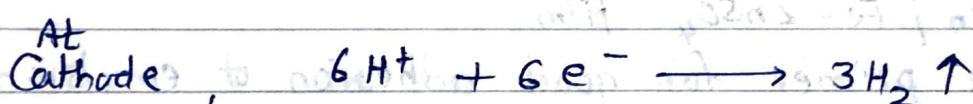
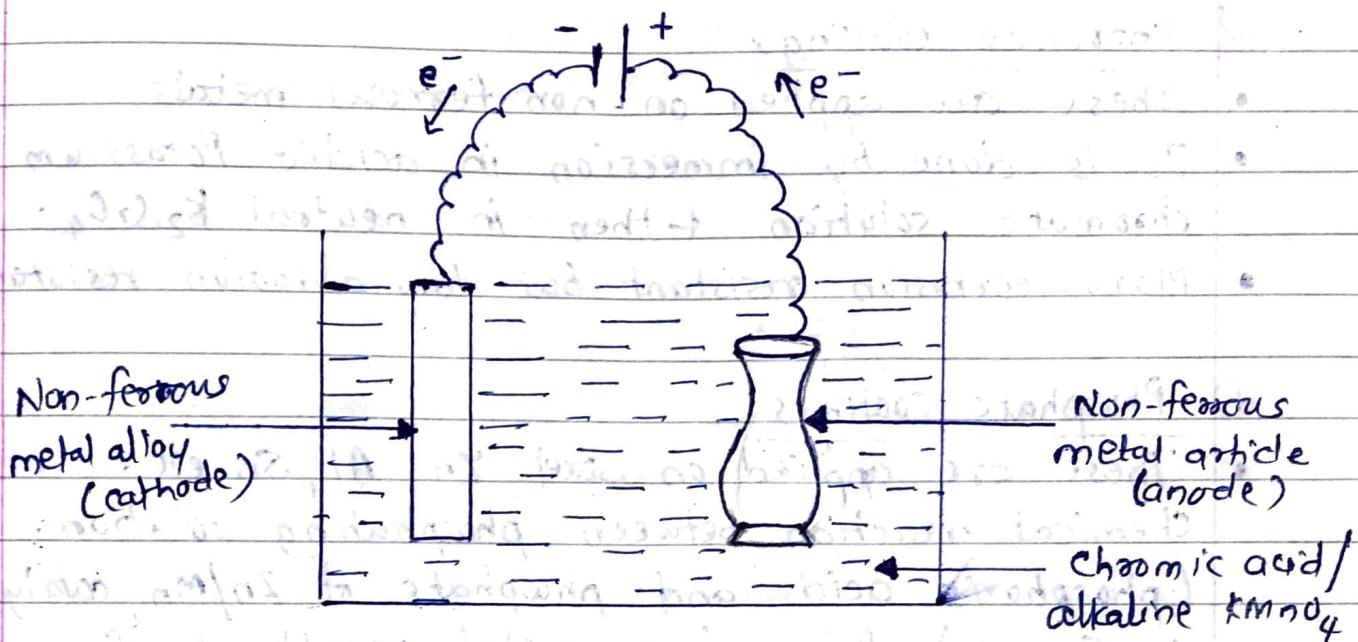
There are 4 types

- a) Anodised Oxide coating
- b) Chemical oxidant coating
- c) Chromate coating
- d)  $\text{PO}_4^{2-}$  (Phosphate) coating

### a) Anodised Oxide Coating

- Produced on non-ferrous metals like Al, Zn, Mg & their alloys.
- Anode  $\rightarrow$  article to be coated
- Cathode  $\rightarrow$  alloy of some metal
- Electrolyte  $\rightarrow$  Chromic acid
- Current is passed for short time.
- Anodic surface gets corroded to form thick coating of metal oxide. Coating is porous.

- Dye is used to seal the pores & it makes metal corrosion resistant.
- $\text{KMnO}_4$ , chromic acid provide nascent  $\text{O}_2$  atoms for oxidation at anode.



↓  
oxide coating

- Anodized coatings are thicker than natural oxide films or staining from iron to anodizing.
- It increases hardness resistance, wear resistance, mechanical strength & electrical insulation property.
- Applications  
 Name plates, ash trays, pens, flower pots, decorative articles.

b) Chemical oxide coatings

- Treating base metal with alkaline oxidizing solution
- Increases corrosion resistance, thickness of original oxide film.

c) Chromate coatings

- These are applied on non-ferrous metals
- It is done by immersion in acidic Potassium chromate solution & then in neutral  $K_2CrO_4$ .
- More corrosion resistant but low abrasion resistant.

d) Phosphate coatings

- These are applied on steel, Zn, Al, Sn etc.  
Chemical reaction between phosphating solution (phosphoric acid and phosphate of Zn/Mn, catalysed by Copper) & base metal results in formation of  $Fe-Mn$  /  $Fe-ZnSO_4$  film.
- Used as primer for good adhesion of emulsion paints.