Unit-3 : Corrosion & its prevention

Lecture Notes (2019) by Mr. V. M. DESAI

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2) Purity of metal
3) Effect of moisture
4) Effect of oxygen (differential aeration principle)
5) Hydrogen overvoltage

Methods of protections of metals from corrosion

B. Sc. Part-III (Sem-V/Paper-VI)

Industrial Chemistry

Academic Year: 2019-20

New Syllabus w.e.f. June-2015

Notes-20/09/2019

"LIFE" AND "TIME" *are the world's Best Teachers.*

Life teaches us to make good use of time and

Time teaches us the value of life.

TEACHING PLAN by V. M. DESAI (2Lectures/Week)

Unit No.	Lect. No.	Topic / Subtopic to be covered	Planned Date	Conducted Date	Teaching Aids Used
2	**Corrosion**		**(6Lectures)**		
	1	Introduction: *Brief idea about COs and POs of this paper, Expected Learning Outcome, Syllabus Contents	23/08/19		
	2	Introduction of corrosion, Electrochemical theory of corrosion,	29/08/19		
	3 **4**	**Factors affecting on corrosion** – i. Position of metals in the EMF series ii. Purity of metal iii. Effect of moisture iv. Effect of oxygen (differential aeration principle) v. Hydrogen overvoltage	30/08/19 & 05/09/19		
	5	**Methods Of Protections** of metals from corrosion	06/09/19		
	6 **7**	Passivity	12/09/19 13/09/19		
	8	**Revision of completed points, Discussion on previous years questions and their answers**	20/09/19		

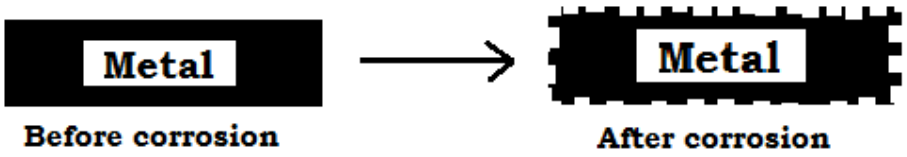
"When you focus on problem, you will have more problems.

But when focus on possibility, you will have more opportunity."

Q. 1) What is corrosion? Give the classification of corrosion. 5M

Ans. Corrosion:

1) **Definition:** Any process of chemical or electrochemical decay or destruction (or deterioration) **of a metal** due to the action of the surrounding medium, is known as Corrosion.
2) Due to corrosion, metal gets converted into unwanted material by the direct chemical reaction or electrochemical reaction of the metal with its surroundings.



(Loss of Metal from its surface)

Classification:

On the basis of nature of corroding medium, corrosion has following two types;

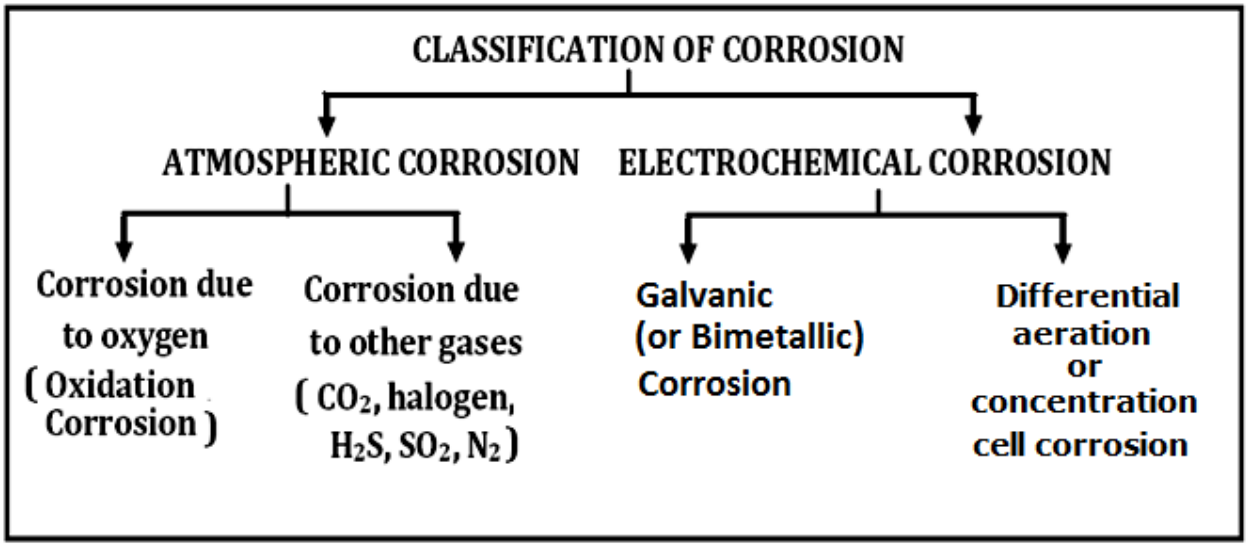
a) Atmospheric corrosion or direct chemical corrosion or dry corrosion and
b) Electrochemical corrosion or wet corrosion or immersed corrosion.

a) Atmospheric corrosion: (Not Imp in Exam)

- **Definition:** When metal comes in contact with atmospheric air, a solid-gas heterogeneous system is formed and corrosion occurring under such conditions is known as **Atmospheric corrosion.**
- **It is also known as dry corrosion.**
- **Causes:** Atmospheric corrosion is caused by direct chemical reaction between metal and surrounding gases. This type of corrosion occurs when metal comes in contact of atmospheric gases such as O_2, CO_2, halogens, hydrogen sulphide, sulphur dioxide, nitrogen etc. at low or high temperature.
- **Example:** 1) Bronze statues get coated with greenish-blue layer.
  2) Silver articles become blackish due to the effect of atmospheric gases.
- **Types of Atmospheric Corrosion :**
  It is further classified into the following two types:
  (i) Corrosion due to oxygen (i.e. Oxidation Corrosion)
  (ii) Corrosion due to other gases
- **Factors affecting on rate of atmospheric corrosion :**
  1) Impurities in the Atmosphere
  2) Presence of suspended impurities in air
  3) Nature of film formed on the metal surface
  4) Effect of Temperature

b) Immersed Corrosion Or Electrochemical corrosion : **(Not Imp in Exam)**

- **Definition:** When metal comes in contact with liquid, a solid-liquid heterogeneous system is formed and corrosion occurring under such conditions is known as **immersed corrosion**.
- **Causes:** Immersed corrosion is caused by the formation of electrochemical cell. This type of corrosion mainly occurs when metal is surrounded by the solution or the aqueous medium.
- **Electrochemical corrosion** is also called as **wet or chemical corrosion**.
- **Example:** 1) Corrosion of water-tanks
  2) Corrosion of sub-marine parts
- **Types of Electrochemical Corrosion :**
  The electrochemical corrosion is classified into the following two types:
  (i) Galvanic (or Bimetallic) Corrosion
  (ii) Differential aeration or concentration cell corrosion.
- **Factors affecting on rate of Electrochemical corrosion :**
  1) Purity of metal
  2) Position of metal in electrochemical series
  3) Effect of Humidity (moisture)
  4) Formation of oxygen concentrated cell
  5) Effect of hydrogen over voltage
  6) pH & temperature



Q. 2) Distinguish between Dry corrosion and Wet or electrochemical corrosion.

	Dry corrosion (Or Atmospheric corrosion)	**Wet corrosion (Or Electrochemical corrosion Or Immersed corrosion)**
1	It occurs in dry atmospheric condition.	It occurs in the presence of moisture or electrolyte.
2	It is due to the direct chemical attack of the metal by the environment.	It is due to electrochemical reaction (i.e. the formation of a large number of anodic and cathodic areas)
3	Rate of corrosion **is slow.**	Rate of corrosion **is high.**
4	Product of corrosion is oxide, chloride, sulphide etc.	Product of corrosion depends on electrolyte and dissolved salts.
5	Corrosion products accumulate at the place of corrosion	Corrosion occurs at the anode while the products are formed elsewhere.
6	Formation of mild scale on iron surface is an example.	Rusting of iron in moist atmosphere is an example.
7	It is a self-controlled process.	It is a continuous process.
8	Even a homogeneous metal surface gets corroded.	Heterogeneous (bimetallic) surface alone gets corroded.
9	It adopts adsorption mechanism.	It follows electrochemical reaction.

"When you focus on problem, you will have more problems.
But when focus on possibility, you will have more opportunity."

Q.3) What is Wet corrosion/Electrochemical corrosion? Explain the corrosion of metal on the basis of electrochemical theory. Imp 5Marks

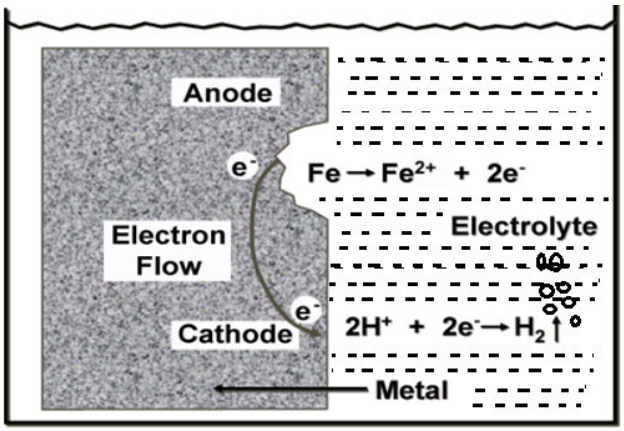
Definition: When metal comes in contact with liquid, a solid-liquid heterogeneous system is formed and corrosion occurring under such conditions is known as wet or electrochemical corrosion.

Electrochemical Theory:

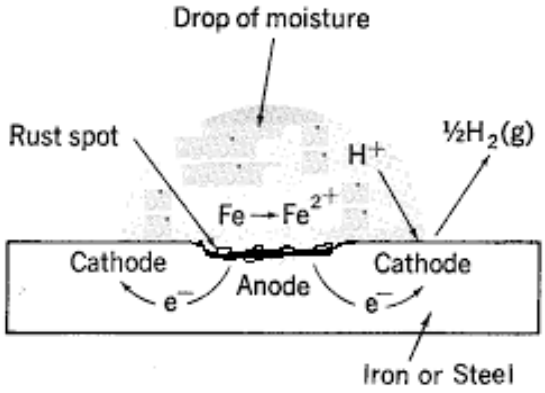
According to this theory (introduced by scientist 'Whitney'), corrosion is **caused by the formation of electrochemical (or Galvanic) cell** where specific area of the metal, which is supposed to be **corroded, acts as an anode** while other area of metal acts as a cathode due to heterogeneity.

The formation of electrochemical (or Galvanic) cell mainly occurs;

1) Due to **'Differential Aeration Principle' where metal surface** exposed to **less oxygen concentration acts as anode** and gets corroded very easily.
2) Due to contact of **two different metals** (metal with **low SRP acts as anode** and has greater tendency to go into solution and gets corroded very easily.



Fig(a)



Fig(b)

(Draw any one diagram for 2marks)

1) **At anode**, metal dissolves by forming ions with liberating electrons.

   Fe ⟶ Fe2+ + 2e- (Loss of electrons i.e. oxidation)

2) **Ionization :** Water (or moisture) which forms a thin film on the surface of metal, gets slightly ionized as, $H_2O \leftrightharpoons H^+ + OH^-$ (Ionization)
3) **At cathode**, these hydrogen ions are reduced by accepting electrons to liberate hydrogen gas.

   $2H^+ + 2e^- \longrightarrow H_2\uparrow$ (Gain of electrons i.e. reduction)

4) <u>Formation of Rust:</u> The Fe^{2+} ions at anode combines with OH^- ions to form ferrous and ferric hydroxide precipitate called as Rust having brown colour.

$$Fe^{++} + 2OH^- \longrightarrow Fe(OH)_2 \downarrow$$
$$Fe^{+++} + 3OH^- \longrightarrow Fe(OH)_3 \downarrow$$

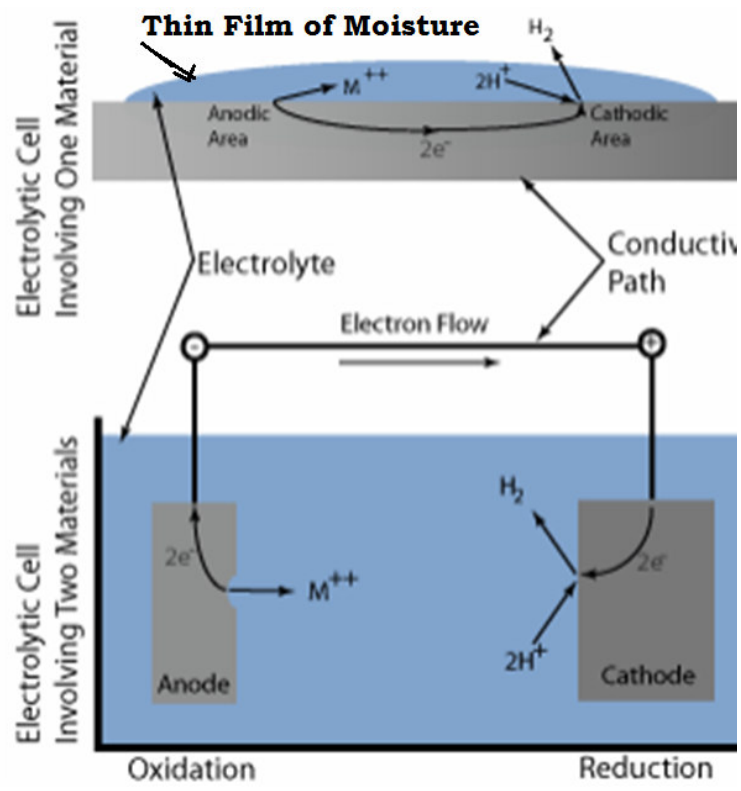
Carbon dioxide from the atmosphere converts the precipitate into hydroxyl carbonate i.e. Rust.

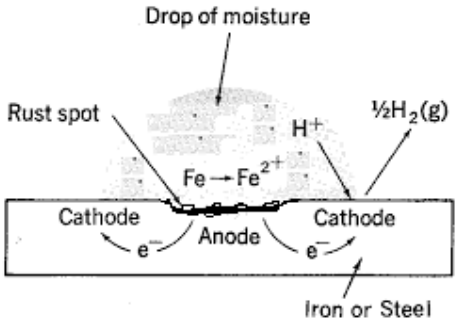
$$Fe(OH)_2 + CO_2 \longrightarrow Fe(OH)HCO_3 \text{ Rust}$$
$$Fe(OH)_3 + CO_2 \longrightarrow Fe(OH)_2HCO_3 \text{ Rust}$$

Remark: Formation of Galvanic or Electrochemical Cell

Metal acts as Anode undergoes corrosion when

1) Metal has **Low SRP** (or High SOP) in electrochemical series.
2) Metal surface area exposed to **less oxygen concentration (i.e. least oxygenated area),**
3) **Oil leakage area (i.e. least oxygenated area),**
4) **Cracks and Unpolished surface** has cavities and crannies,
5) Metals under strain becomes anodic in nature





Factors affecting rate of corrosion MIMP 10Marks

Q. 4) Write notes on: Factors affecting rate of corrosion. 10M SU May-2012,2008 MIMP

OR What are the different Factors affecting on rate of corrosion? Explain in detail. 10M SU-Dec.2011, 2012, 2016, 2017, 2018

Ans. **Factors affecting the Rate of Corrosion**

A) Nature of Metal

1) **Purity of metal**
2) **Position of Metal in EMF series**
3) **Hydrogen over voltage**
4) **Area effect (Anodic & Cathodic Area)**
5) **Nature of the oxide layer or protective layer**
6) **Solubility of oxide product**

B) Nature of Medium (Environment)

1) **Temperature**
2) **Humidity (% of moisture)**
3) **pH of the medium**
4) **Conductance of corroding medium**

A) Nature of the metal:

1) Position of Metal in Electrochemical series on the basis of SRP:

i) The rate of corrosion depends on the **relative position of the metal** in electrochemical series.

ii) When the two dissimilar metals are in contact with an electrolyte, then the ***metal with low SRP*** (or high SOP or at higher position in electrochemical series) has greater tendency to go into solution and ***gets corroded very easily.***

iii) On the other hand, ***metal with high SRP*** (or low SOP) has little tendency to go into solution and hence they are not corroding.

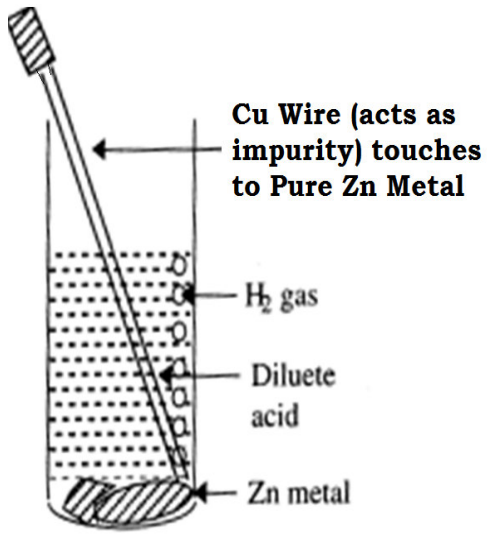
iv) Similarly, if the two metals are much apart in electrochemical series then ***corrosion of anodic metal is greater or faster.***

2) Purity of the metal:

i) Impurities in a metal cause heterogeneity and forms the galvanic cell in aqueous medium and hence the anodic parts get corroded.

ii) *If the impurity element has high SRP (or low SOP) then* ***it acts as a cathode*** *whereas* ***base metal acts as anode*** *and hence base metal gets corroded*.

iii) Thus, the rate of electrochemical corrosion depends on purity of metal.



For example:

In case of pure Zn metal when reacts with dil. Acid then H_2 gas is not evolved and **Zn remains undissolved state** because **galvanic cell is not formed**.

But in case of Cu wire touches to Pure Zn metal then Zn acts as anode and Cu wire acts a cathode i.e. **it forms a galvanic cell which causes corrosion of Zn.**

3) Hydrogen over-voltage:

$$\textit{Hydrogen over-voltage} = \left[\begin{array}{c}\textit{Potential required to evolve hydrogen at surface of given metal (acts as anode)}\end{array}\right] - \left[\begin{array}{c}\textit{Potential required to evolve hydrogen at Pt electrode (acts as cathode)}\end{array}\right]$$

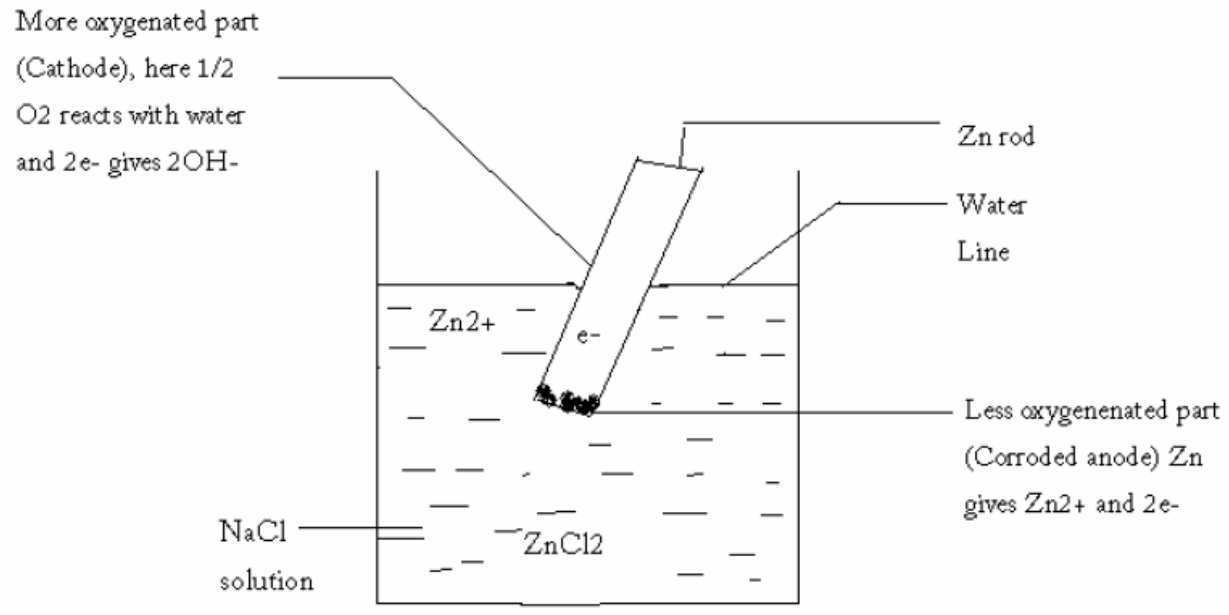
The presence of impurities with **low hydrogen over voltage increases** the rate of corrosion while the presence of impurities with high hydrogen over voltage reduces or stop the rate of corrosion of a metal.

4) **Effect of Oxygen**: (**Differential Aeration Principle**)

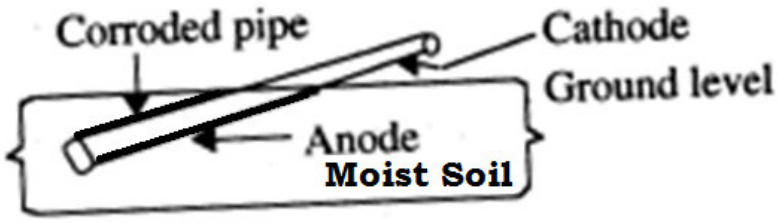
The effect of oxygen on corrosion of the metal mainly based on **'Differential Aeration Principle'.** This principle may be stated as the part of the metal having more restricted access for oxygen (least oxygenated area) becomes anodic w.r.t. remaining part and gets corroded.

For Examples:

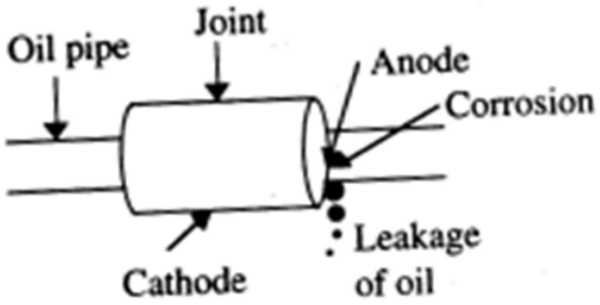
a) If a metal is partially immersed in a conducting solution, the metal part above the solution is more aerated and becomes cathodic. The metal part inside the solution is less aerated (i.e. (least oxygenated area) and thus becomes anodic and suffers corrosion.



b) Due to Differential Aeration Principle, pipelines passing through **moist soil becomes anodic** to those parts which are passing through dry soil and hence **gets corroded** due to less availability of oxygen in moist soil.

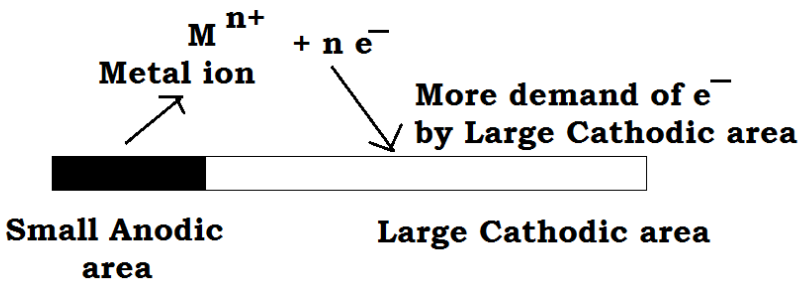


c) Due to Differential Aeration Principle, oil pipe lines corrode **at the joints where there is slight leakage of oil.** This leakage parts acts as anode due to less availability of oxygen and hence gets corroded first.



5) Effect of Area:

When **anodic metal area is smaller** than cathodic area, rate of corrosion at **anode is higher** because of demand of electron by large cathodic area.



B) Nature of the environment:

1) Temperature: Rise of temperature increases the rate of corrosion.

2) Effect of Humidity (Or Effect of % of moisture) :

The rate of corrosion will be more when the relative humidity (% of moisture) of the environment **is high**. The moisture acts as a solvent for oxygen, carbon dioxide, sulphur dioxide etc. in the air to **produce the electrolyte** which is required for setting up a **electrochemical cell (or** galvanic cell) by which corrosion occurs to a great extent.

3) pH value of corroding medium: (Not IMP in Exam)

i) The corrosion of metals **affected by the pH value** of the surrounding medium.

ii) For example the rate of corrosion of zinc is **slow in alkaline medium** and rate of corrosion of aluminum is ***slow in acidic medium***.

Questions:

1) State and explain differential aeration principle of corrosion with suitable example. 5Marks
2) What is corrosion? Explain different factors affecting on rate of corrosion. 10Marks
3) Explain following different factors affecting on rate of corrosion' 10Marks **MIMP**
   a) Position of metal in electrochemical series
   b) Effect of Hydrogen Over Voltage
   c) Effect of Oxygen (Differential Aeration Principle)
   d) Effect of Moisture
   e) Purity of Metal

4) What is corrosion? Mention different methods of protection of metals (prevention of corrosion). Explain any two methods based on treatment of metals. **10Marks IMP**

OR Define corrosion. Explain any two methods of protection of metals from corrosion.

Prevention Methods of corrosion MIMP 10Marks

a) By Proper Design and Material Selection (Not Imp in exam)

b) By Cathodic Protection **(IMP in Exam)**

i) Sacrificial method

ii)Impressed current method

c) Application of Metallic Coating; **(IMP in Exam)**

i) Hot dipping

ii) Metal cladding

iii)Metal spraying and

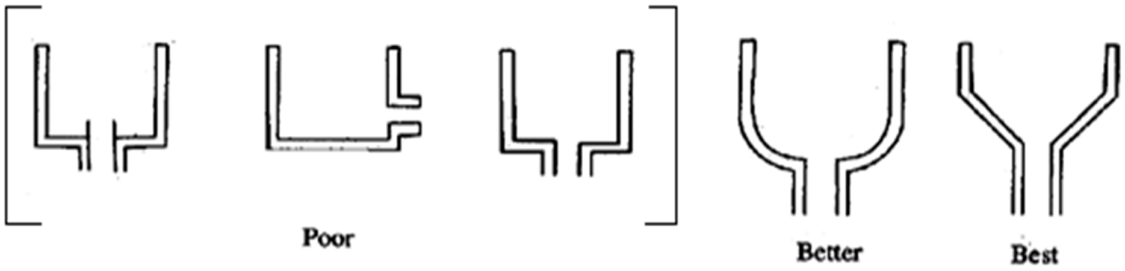
iv) Electroplating

d) By using Corrosion Inhibitors

e) By protective non-metallic coatings (Not IMP in Exam)

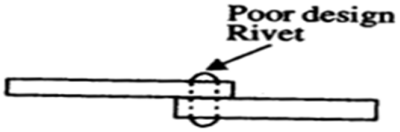
Method-1: By Proper Design and Material Selection:

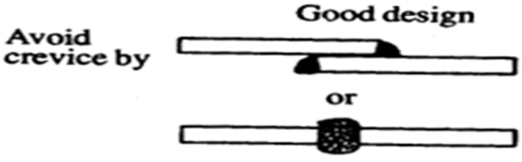
1) Proper design in case of drainage system:



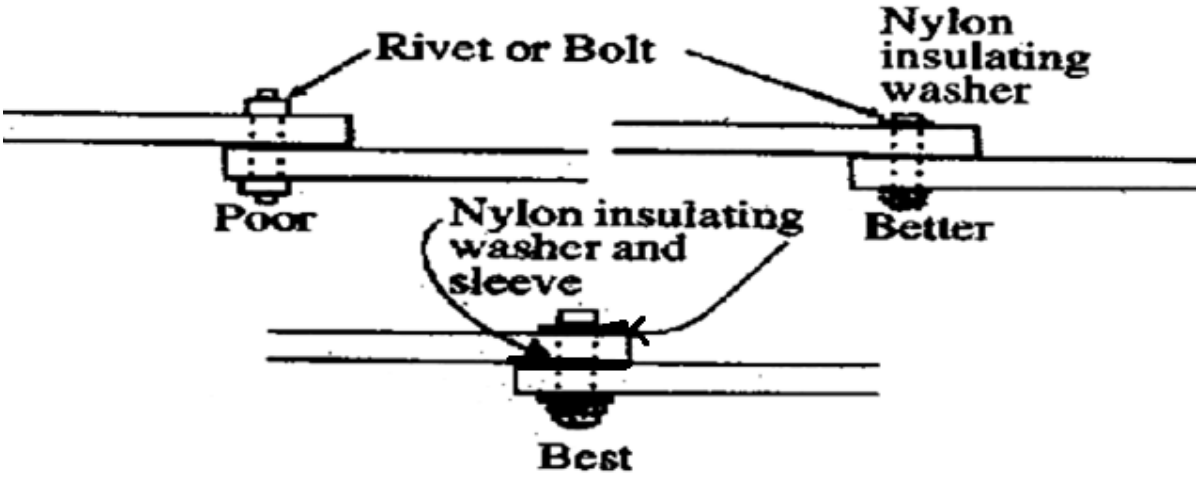
The design must avoid more complicated shapes having more angles, edges, corners etc.

2) The bolts and rivets should be replaced **by proper welding.** It is as shown in fig.





3)Insulation avoids galvanic corrosion



4) Removal of strain: Metals under strain becomes anodic in nature which enhances corrosion. Hence, metals free from strain should be used to avoid corrosion.

5) Polishing of surface: Metal surface should be properly polished one. Unpolished surface has cavities and crannies. Due to differential aeration principle, space of cavities and crannies acts as anode and hence corrodes.

6)<u>By proper Material Selection (i.e. Choice of metals and alloys):</u>

a) The first choice is **to use noble metals** such as gold and platinum. They are most resistant to corrosion. As they are precious, they cannot be used for general purposes.

b) The next choice is **to use purest possible metal**. But in many cases, it is not possible to produce a metal of high chemical purity. Hence, even a trace amount of impurity leads to corrosion.

c) Thus, the next choice is the **use of corrosion resistant alloys.** Several corrosion resistant alloys have been developed for specific purposes and environment.

For example,

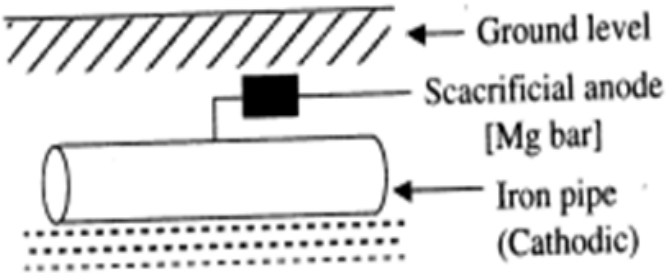
(i) Cupro-nickel (70% Cu + 30%Ni) alloys are now used for condenser tubes and in fractionating column in oil refineries.

(ii) Highly stressed Nimonic alloys (Ni-Cr-Mo alloys) used in gas turbines are very resistant to hot gases.

Method-2 : By Cathodic Protection:

In this method, force the metal to be protected to behave like cathode to avoid corrosion.

i) **Sacrificial Anodic Protection:** Metal to be protected from corrosion connected to other more anodic metal like Mg or Zn, this anodic metal goes on disappearing and thus saves the cathode form rusting.
e.g. By using Sacrificial anodic protection method, rusting of iron article is stopped by connecting anodic metals like Zn, Mg, Al etc. by wire.

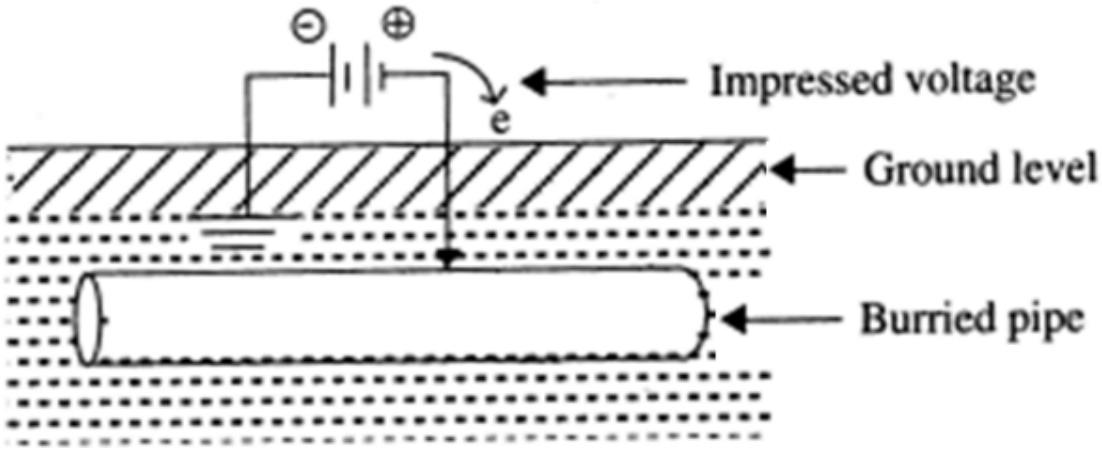


(Draw diagram in exam)

Image of Sacrificial Anodic Protection

ii) Impressed Current method:

Direct current is applied in opposite direction to nullify the corrosion current which converts the corroding metal from anode to cathode.

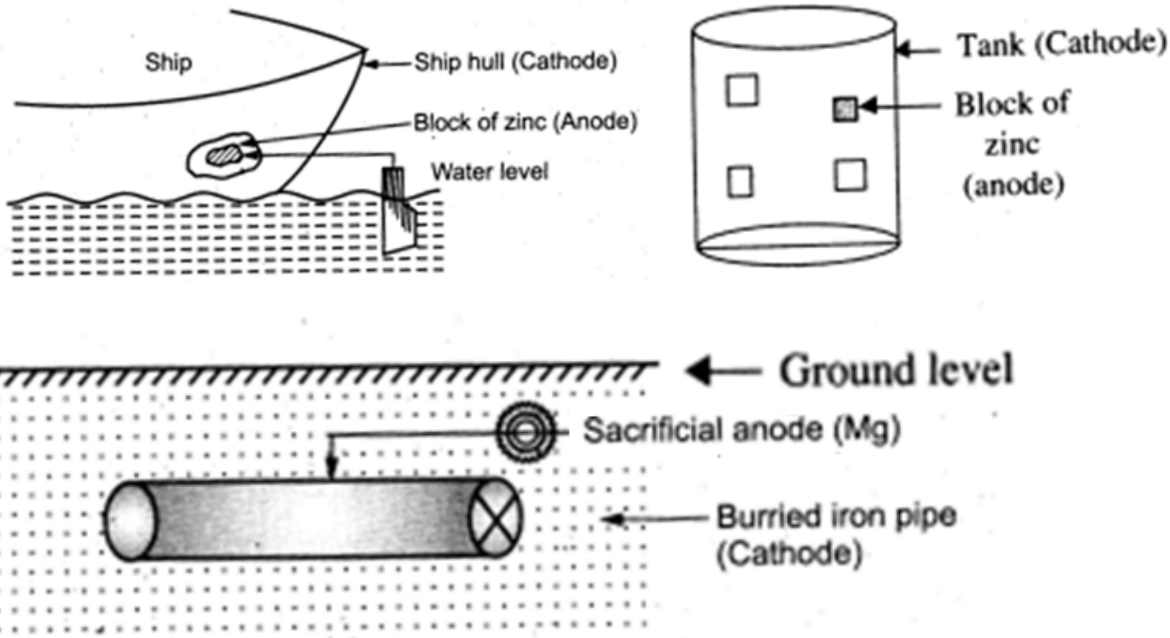


(Draw diagram in exam)

Applications of Cathodic Protection:

1. Insertion of magnesium sheets into the domestic water boilers to prevent the formation of rust.
2. Protection as buried pipelines, underground cables from soil corrosion.
3. Protection from marine corrosion of ship hulls, cables, piers etc.

Following diagrams are not expected *in exam, it is only for understanding the concept*



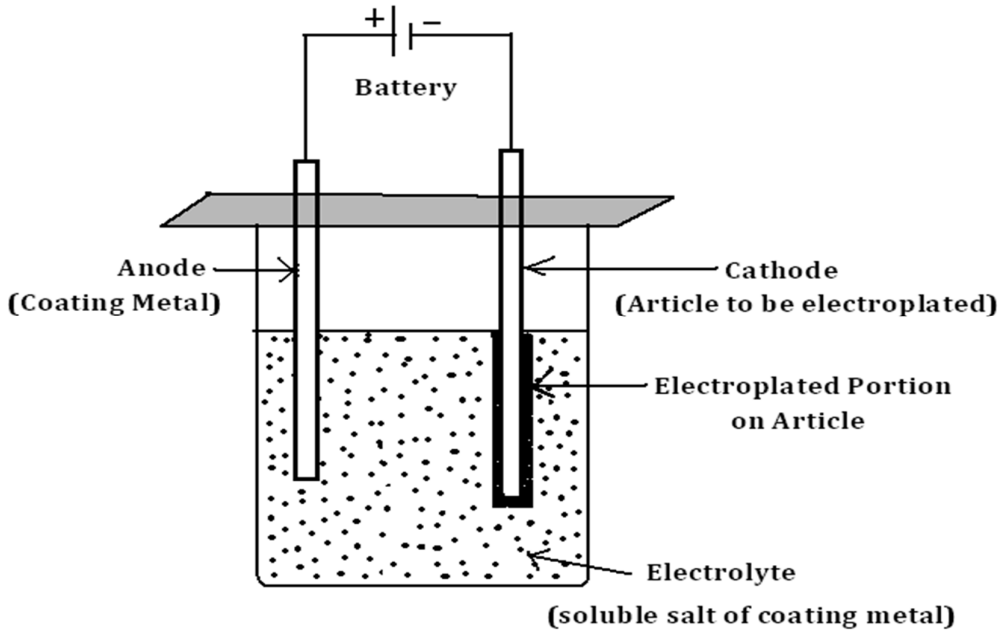
Comparison between Sacrificial anode method & Impressed current cathodic method

(Not in syllabus, only for understanding concept)

Sl. No.	Sacrificial Anode method	Impressed Current method
1/	External power supply is not required.	External power supply is required.
2/	The cost of investment is low.	The cost of investment is high.
3/	This requires periodic replacement of sacrificial anode.	Replacement is not required as anodes are stable.
4/	Soil and microbiological corrosion effects are not considered.	Soil and microbiological corrosion effects are taken into account.
5/	This is the most economical method especially when short term protection is required.	This is well suited for large structures and long term operations.
6/	This is a suitable method when the current requirement and the resisitivity of the electrolytes are relatively low.	This is a suitable method even when the current requirement and the resistivity of the electrolytes are high.

Method-3: Applications of Metallic Coating:

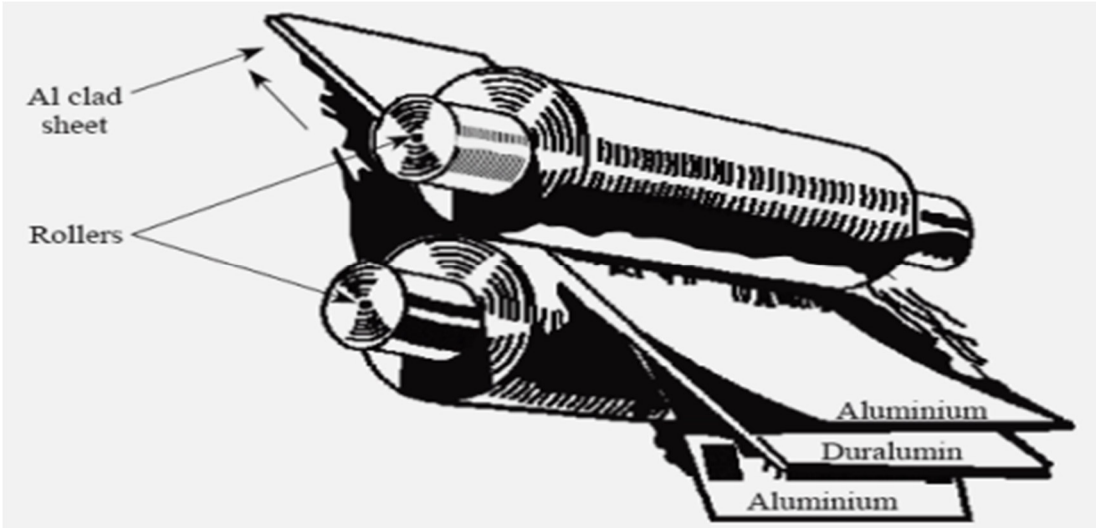
i) **Electroplating:** By the process of electrolysis a thin film of coating metal like nickel, chromium, copper or zinc is deposited on the surface to be protected. The surface to be protected is made the cathode and the coating metal to be deposited is made the anode.



(Draw above diagram in exam)

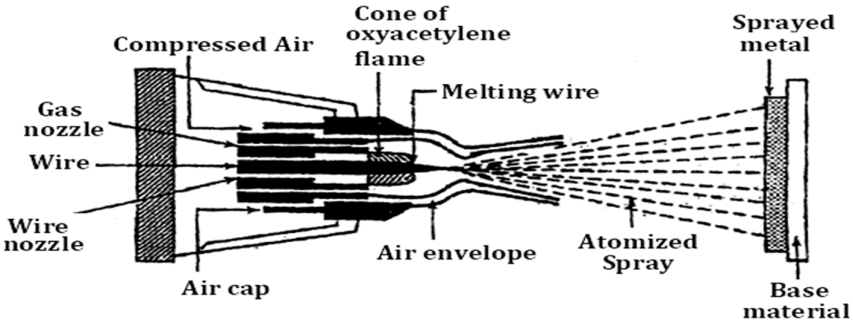
ii) **Metal Cladding:** The base metal to be protected and coating metal are sandwiched by pressing through rollers under the action of heat & pressure.

E.g. Alclad Sheeting– Plate of duralumin is sandwiched between 99.5%pure aluminum



(In exam, diagram is not necessary => it is only for understanding)

iii) Metal spraying: The coating metal in molten state is sprayed on base metal by means of spraying gun (***spraying device***).
e.g. Aluminum is plated in this way on Aircrafts.

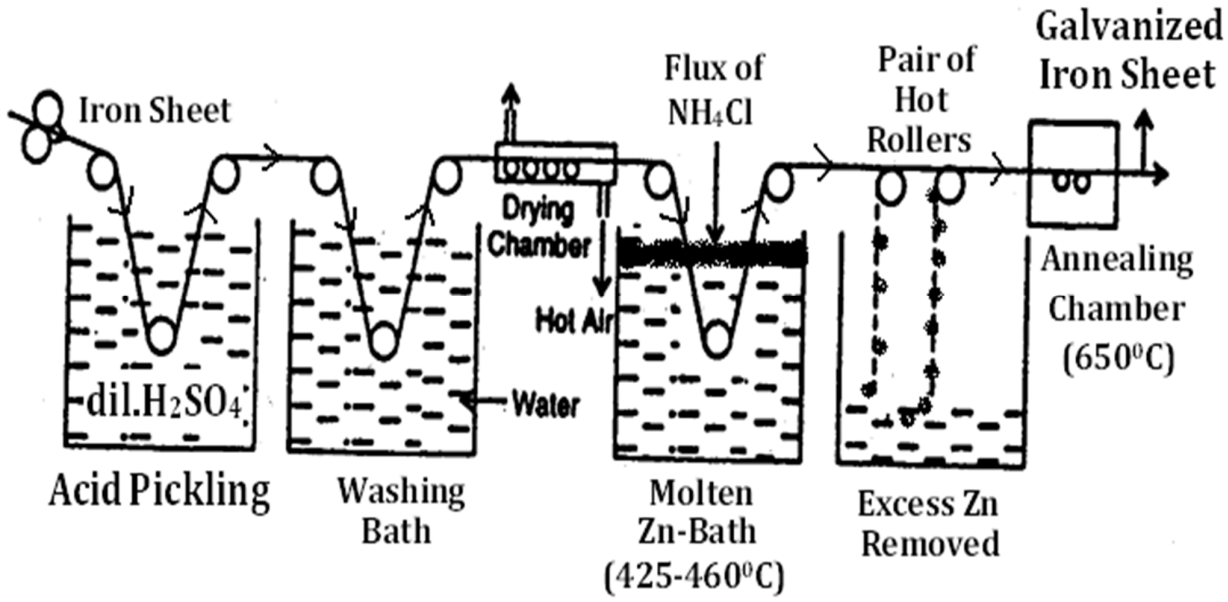


(In exam, diagram is not necessary => it is only for understanding)

iv) Cementation: The base metal to be protected is heated with powdered coating metal to promote the diffusion of coating metal into the base metal and hence a layer of alloy is formed which prevent its corrosion. E.g. when chromium is used as a coating metal for steel surface, the process is called chromising.

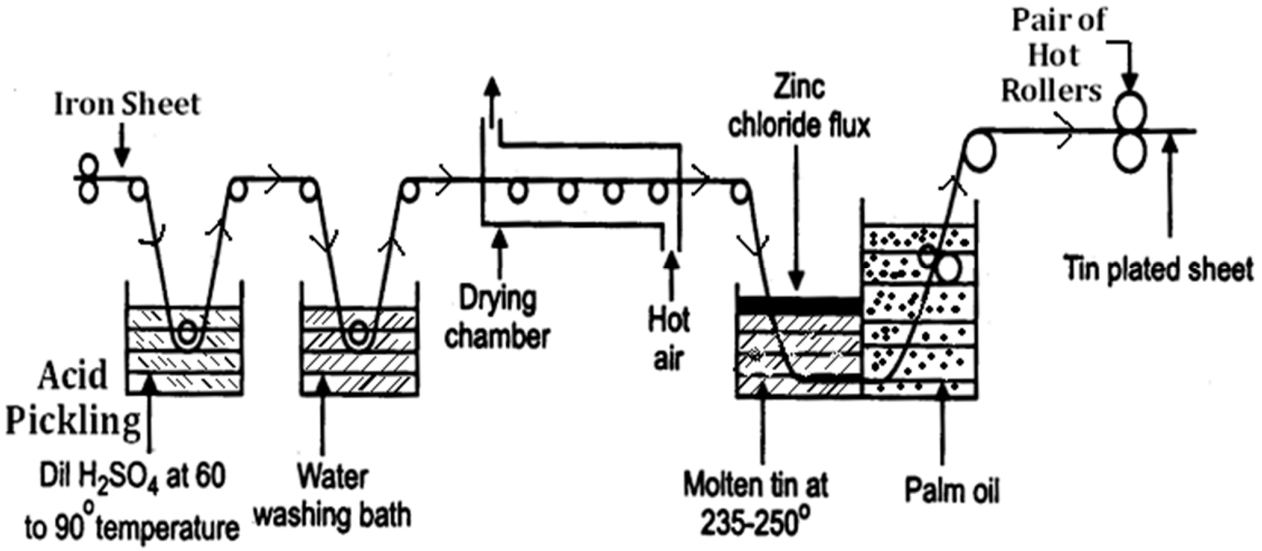
v) Hot Dipping: The base metal to be coated is immersed in a bath of the molten coating metal. For examples;

a) Galvanizing: After cleaning the surface of article with acid wash followed by wash with clean water and drying, article to be protected from corrosion is dipped in a bath of molten zinc. A fine film of zinc that get deposited protect the surface from contact with atmosphere and consequence oxidation. Covering the iron article with Zinc is Galvanization.



(In exam, diagram is not necessary => it is only for understanding)

b) Tin plating: After cleaning the surface with acid wash followed by wash with clean water and drying, it is dipped in a bath of molten tin. A fine film of tin that get deposited protect the surface from contact with atmosphere and consequence oxidation.



(In exam, diagram is not necessary => it is only for understanding)

Method-4: By using Corrosion Inhibitors:

- Using certain chemical substances known as corrosion inhibitors can reduce corrosion rate when added in small quantity.

• **Types of inhibitor:**

i) Anodic Inhibitor: inhibits corrosion of anode

e.g. Some inorganic salts like metal silicate & borates

ii) Cathodic Inhibitor: inhibits corrosion of cathode

e.g. Some reducing agents like sodium thiosulphate & some salts of Ni, Mg etc.

Method-5: By using inert/unreactive Protective Coatings:

The most common method of protection is simply painting the metal object.

However, coatings such as concrete, plastic (PVC), fibreglass, rubber and bitumen can also be used. They all simply stop the oxygen and/or the water from coming into contact with the metal.

The main problem with this method is if you scratch the protective coating. The iron will begin to corrode and will lift off even more of the protective surface.

For examples:

- Coating of oil, grease can be used to give a temporary protective coating
- Organic polymers or rubber latex can be applied to give coatings which can be stripped off when required
- **Painting:** Paints usually the lead paints are applied on the surface to be protected. Exposed metal surfaces as in case of roof and bridge structure are given this treatment which has to be repeated after regular interval of time.
- **Phosphate Coating :** An insoluble protective layer of ferric phosphate is obtained on the surface of iron by dipping it in phosphoric acid which adheres to the metal surface tenaciously and protect the metal from corrosion.

END

Case Studies of Corrosion Failure (Beyond Syllabus)

1) **Aloha Incident:** In 1988, 19-year old Boeing 737 operated by Aloha Airlines lost a major portion of the upper fuselage in full flight at 24000 ft

Aloha Incident

"Only I Can Change My Life. No One Can Do It for Me."

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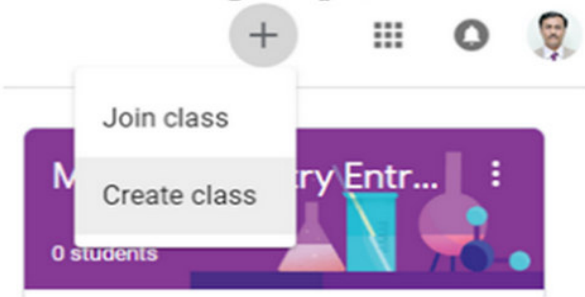

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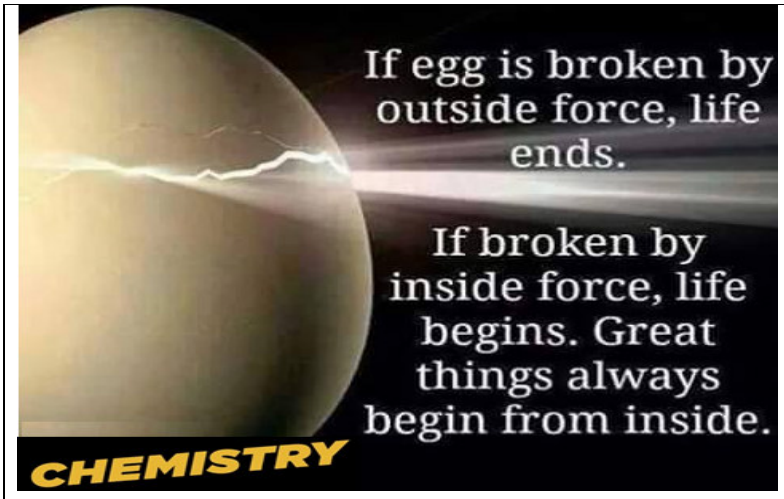

Be positive to your goals

"Without Your Involvement You Can't Succeed.

With Your Involvement You Can't Fail.

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