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UNIT V

Phase equilibrium and corrosion

Phase- It is defined as any homogeneous, physically distinct and mechanically separable portion of a system, which is separated from other such parts of the system by definite boundary surfaces in a system.

Component- It is defined as the smallest number of independently variable constituents taking part in the state of equilibrium by means of which the composition of each phase can be expressed directly or in the form of chemical equation.

Degree of freedom- It is defined as the minimum number of the independently variable factors such as the temperature, pressure and composition of the phases which must be arbitrarily specified in order to represent perfectly the condition of a system.

PHASE RULE

Gibbs' phase rule was proposed by Josiah Willard Gibbs . The rule applies to non-reactive multi-component heterogeneous systems in thermodynamic equilibrium and is given by the equality .

$$F = C - P + 2$$

where F is the number of degrees of freedom, C is the number of components and P is the number of phases in thermodynamic equilibrium with each other.

The number of degrees of freedom is the number of independent intensive variables, i.e. the largest number of thermodynamic parameters such as temperature or pressure that can be varied simultaneously and arbitrarily without determining one another. An example of one-component system is a system involving one pure chemical, while two-component systems, such as mixtures of water and ethanol, have two chemically independent components, and so on. Typical phases are solids, liquids and gases.

Uses of Phase Rule : -

- With the help of terms phases , components and degrees of freedom the phase rule gives a convenient basis for classification of equilibrium state of system.
- The information about molecular structure is not necessary because It applies to macroscopic systems .
- The phase rule shows that various systems having same degrees of freedom behave in a similar fashion .
- It helps in deciding whether the given number of substances together would exist in equilibrium under a given set of conditions

Limitations of phase rule : -

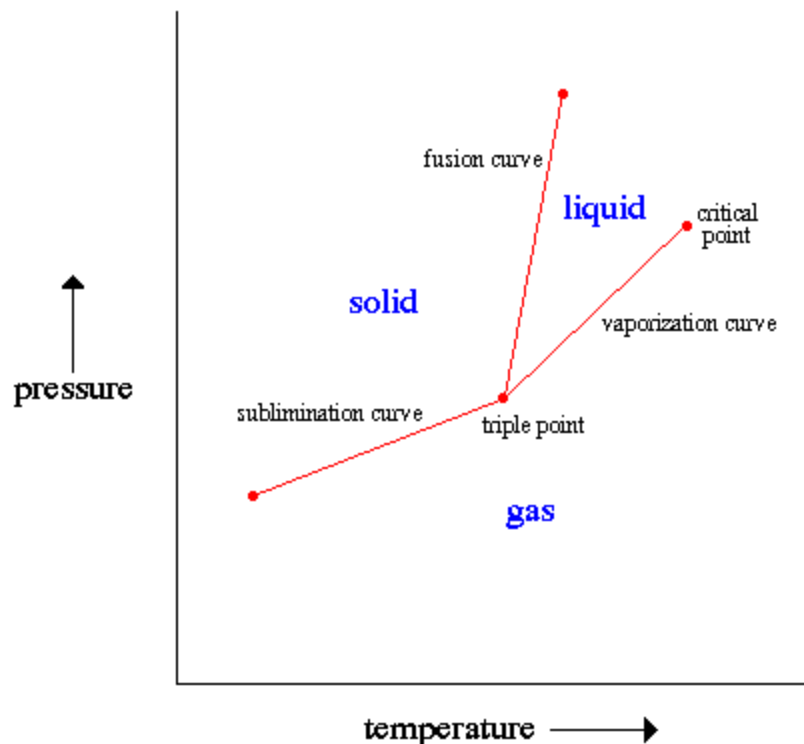
- Not applicable for the systems which are slow in reaching to equilibrium state .
- There is no consideration of magnetic and electric influence since system is defined only the variables like pressure temperature and components force.

- Any liquid or solid present should not be in finally divided state otherwise the value of their vapor pressure will differ from their normal value .

Phase equilibrium – it refers to the set of conditions where more than one phase may exist. It can be reflected by constancy with time in the phase characteristics of a system. In most metallurgical and materials systems, phase equilibrium involves just solid phases. However the state of equilibrium is never completely achieved because of very slow rate of approach of equilibrium in solid systems. This leads to non-equilibrium or meta-stable state, which may persist indefinitely and of course, has more practical significance than equilibrium phases. An equilibrium state of solid system can be reflected in terms of characteristics of the microstructure, phases present and their compositions, relative phase amounts and their spatial arrangement or distribution.

A **phase diagram** in physical chemistry, engineering, mineralogy, and materials science is a type of chart used to show conditions (pressure, temperature, volume, etc.) at which thermodynamically distinct **phases** occur and coexist at equilibrium. Common components of a phase diagram are lines of equilibrium or phase boundaries, which refer to lines that mark conditions under which multiple phases can coexist at equilibrium. Phase transitions occur along lines of equilibrium.

A phase diagram is a graph showing the limiting conditions for solid, liquid, and gaseous phases of a single substance or of a mixture of substances while undergoing changes in pressure and temperature or in some other combination of variables, such as solubility and temperature. The figure shown below displays a typical phase diagram for a one-component system (i.e., one consisting of a single pure substance), the curves having been obtained from measurements made at various pressures and temperatures.



Phase diagrams are specific for each substance and mixture. Complex mixtures may require three-dimensional phase diagrams, which can be represented in two dimensions through use of perspective. Phase diagrams are widely used in studies of mineral equilibria in connection with the conditions of formation of rocks and minerals within the Earth. They also are invaluable when designing industrial equipment and seeking optimum conditions for manufacturing processes, and in determining the purity of substances.

Phase diagrams illustrate the variations between the states of matter of elements or compounds as they relate to pressure and temperatures. The following is an example of a phase diagram for a generic single-component system:

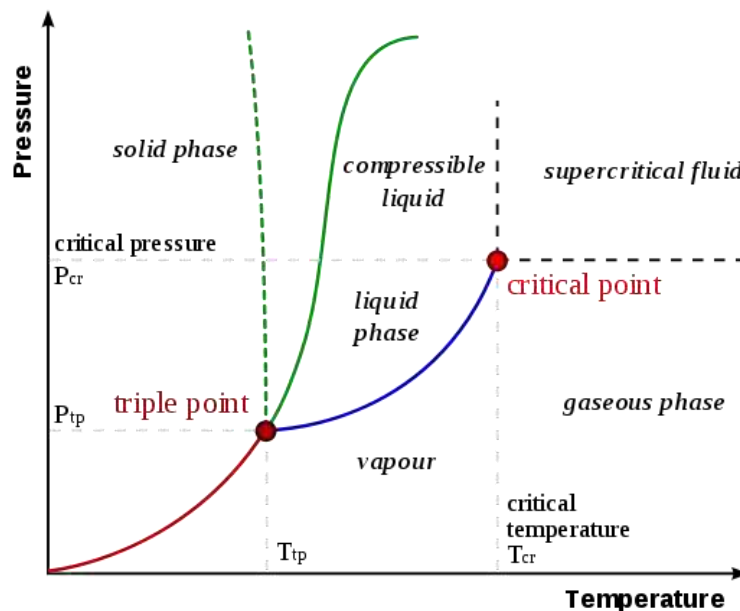


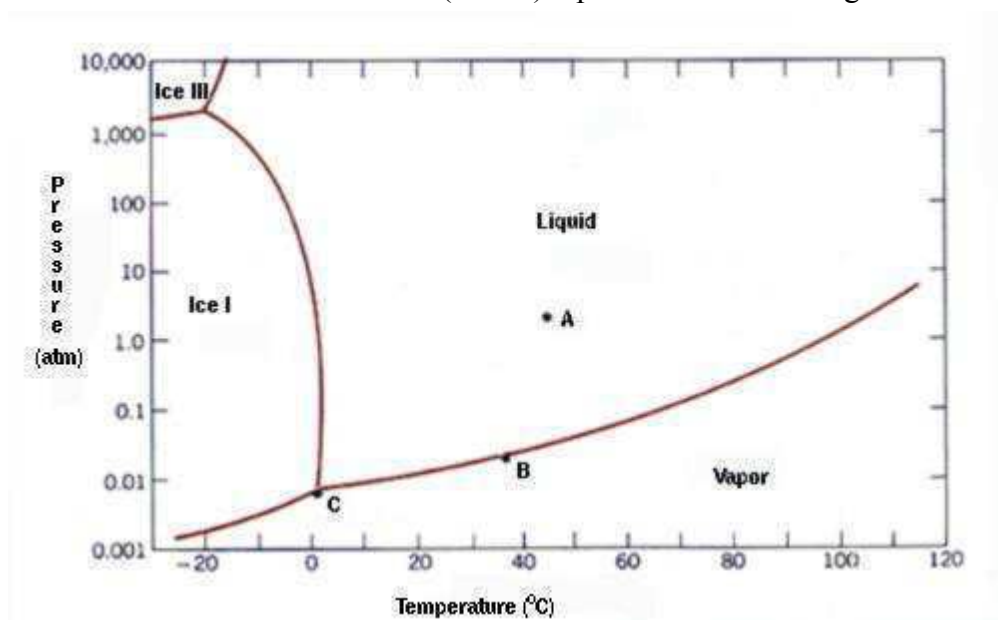
Figure 1. General Phase diagram

- **Triple point** – the point on a phase diagram at which the three states of matter: gas, liquid, and solid coexist
- **Critical point** – the point on a phase diagram at which the substance is indistinguishable between liquid and gaseous states
- **Fusion(melting) (or freezing) curve** – the curve on a phase diagram which represents the transition between liquid and solid states
- **Vaporization (or condensation) curve** – the curve on a phase diagram which represents the transition between gaseous and liquid states
- **Sublimation (or deposition) curve** – the curve on a phase diagram which represents the transition between gaseous and solid states

Binary diagrams: These diagrams constitute two components, e.g.: two metals (Cu and Ni), or a metal and a compound (Fe and Fe_3C), or two compounds (Al_2O_3 and Si_2O_3), etc. In most engineering applications, as mentioned before, condensed phase rule is applicable. It is assumed that the same is applicable for all binary diagrams, thus the presentation of binary diagrams becomes less complicated. Thus binary diagrams are usually drawn showing variations in temperature and composition only. It is also to be noted that all binary systems consist only one liquid phase i.e. a component is completely soluble in the other component when both are in liquid state. Hence, binary systems are classified according to their solid solubility. If both the components are completely soluble in each other, the system is called isomorphous system. E.g.: Cu-Ni, Ag-Au, Ge-Si, Al_2O_3 - Cr_2O_3 . Extent solid solubility for a system of two metallic components can be predicted based on Hume-Ruthery conditions, summarized in the following: - Crystal structure of each element of solid solution must be the same. - Size of atoms of each two elements must not differ by more than 15%. - Elements should not form compounds with

each other i.e. there should be no appreciable difference in the electro-negativities of the two elements. - Elements should have the same valence.

Isomorphous system: Figure-2 depicts a typical phase diagram for an isomorphous system made of two metallic elements A and B. As cited earlier, any phase diagram can be considered as a map. A set of coordinates – a temperature and a composition – is associated with each point in the diagram. If the alloy composition and temperature specified, then the phase diagram allows determination of the phase or phases that will present under equilibrium conditions. There are only two phases in the phase diagram, the liquid and the solid phases. These single-phases regions are separated by a two-phase region where both liquid and solid co-exist. The area in the figure-2 above the line marked liquids (A'B'B') corresponds to the region of stability of the liquid phase, and the area below the solidus line (A'dB') represents the stable region for the solid phase.



CORROSION

Corrosion is defined as “the destruction or deterioration and consequent loss of metals or alloys through chemical or electrochemical attack by the surrounding environment”.

The primary factors that initiate corrosion on metals are atmospheric air, water and also conducting surface of the metal.

Egs: Rusting of iron, green scales are formed on copper vessels

Corrosion of metal occurs either by direct chemical attacks or by electrochemical attack on the metal by the corrosive environment.

If the corrosion takes place due to direct chemical attack (in the absence of moisture) that type of corrosion is known as dry corrosion.

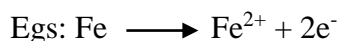
If the corrosion of metal takes place due to electrochemical attack in presence of moisture or a conducting medium such corrosion is known as wet corrosion or electrochemical corrosion.

Electrochemical theory of corrosion: Most of the corrosion takes place on the basis of electrochemical reactions on the surface of metal such a type of corrosion is known as wet corrosion. Electrochemical theory of corrosion can be taking iron as an example.

When a metal like iron is exposed to the environment according to electrochemical theory corrosion of metal takes place due to the formation of anodic and cathodic regions on the same metal surface or when the two metals are in contact with each other in a corrosive medium. These anodes and cathodes are formed due to the heterogeneities at the interfaces of the metal and environment. The heterogeneities on a metal surface could develop due to several factors like

1. On a metal surface if the concentration of the oxygen is different (if in the metal the area which is exposed to more oxygen acts as cathode, the area which is exposed to less oxygen concentration acts as anode).
2. Due to contact of two different metals (egs: if copper and iron are in contact with each other, then Fe acts as anode and copper acts as cathode due to change in electrode potential).
3. If metal surface subjected to stress (area under stress acts as anode).

Thus anodic and cathodic area are formed, in presence of corrosion medium (like moisture etc.) At anode oxidation takes place so that metal is converted into metal ions with the liberation of electrons.

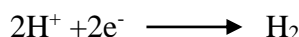


At the cathodic regions, reduction takes place since the metal at cathodic region cannot be reduced further, so some constituents of the corrosive medium take part in the cathodic reaction. Since in the cathodic reaction as the constituents of the corrosion medium are involved, they are more complicated and dependent on the nature of environment. Most common type of cathodic reaction are 1. Liberation of hydrogen 2. Absorption of oxygen.

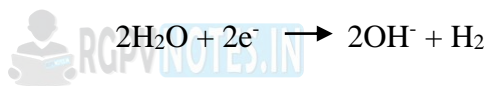
Cathodic reactions:

(a) Liberation of Hydrogen type

- (i) If the medium is acidic and in the absence of O_2

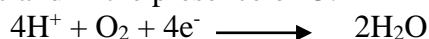


- (ii) If the medium is neutral or alkaline in the absence of O_2 .

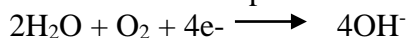


(b) Absorption of oxygen type

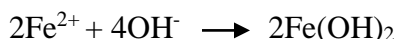
- (i) If the medium is acidic and in the presence of O_2 .



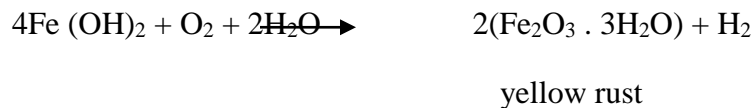
- (ii) If the medium is neutral or alkaline and in the presence of O_2 .



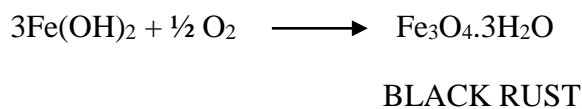
The metal ions (Fe^{2+}) liberated at anode and some anions (OH^-) formed at cathode diffuse towards each other through the conducting medium and form a corrosion product some where between the anode and cathode as



In an oxidizing environment, the insoluble Fe(OH)_2 oxidised to ferric oxide as following reaction.



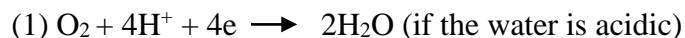
if the concentration of oxygen is limited then Fe(OH)_2 is converted into magnetic oxide of Fe and is known as black rust.



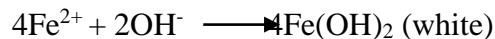
Mechanism of CORROSION : - The anodic reaction would be



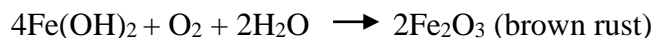
The loss of electrons leaves positively charged ions at the anode which travel from the anode to cathode via the water and carry the positive current. The electrons which are released on the anode travel from the anode to the cathode via the metallic circuit. These electrons are utilized in the reduction of oxygen present in water which is in contact with the cathode. Hence, at the cathode, one of the following reactions may take place.



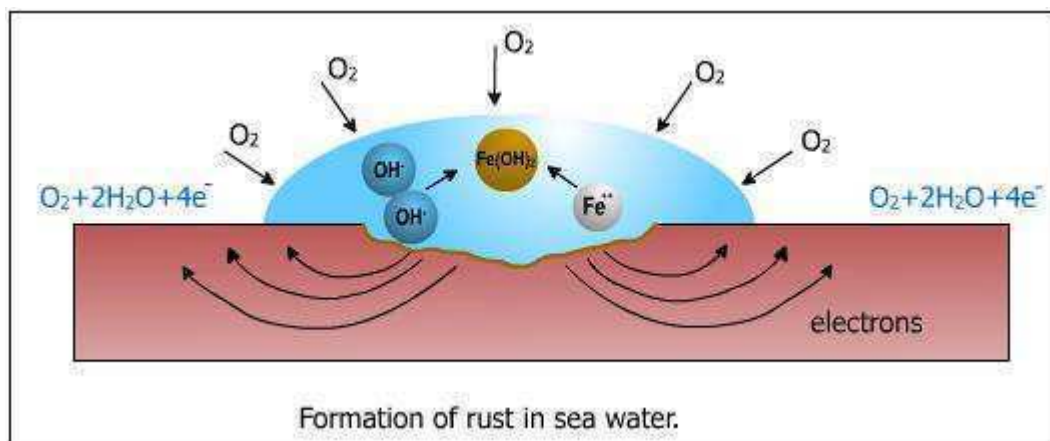
The negatively charged OH^- ions react with the positively charged Fe^{2+} ions and forms Fe(OH)_2 .



OR



The end product is Fe_2O_3 , which is generally called "rust". The rust is formed a little away from the surface. The mechanism of rust formation is shown in the following figure.



Types of Corrosion: Corrosion on the metals taking place depending on the nature of metals and depending on the types of environment by different mechanisms, giving different types of corrosion.

1 Galvanic corrosion or differential metal corrosion:

This occurs when two dissimilar metals are in contact with each other in a corrosive conductive medium; a potential difference is set up resulting in a galvanic current. The two metals differ in their tendencies to undergo oxidation. The metal with lower electrode potential or more active metal acts as anode and the metal with higher electrode potential acts as cathode. The potential difference is main factor for corrosion to take place. The anodic metal undergoes corrosion where as cathodic metal gets un-attacked.

Ex: When iron contact with copper iron has lower electrode potential acts as anode and undergoes oxidation as,



Whereas copper which is having higher electrode potential acts as cathode gets unaffected. The rate of galvanic corrosion depends upon potential difference between anodic and cathodic

metals, ratio of anodic and cathodic area and environmental factors and tendency of the metal to undergo passivity etc.

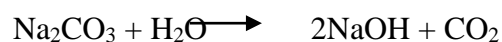
Other example : When Fe contact with Sn then Fe acts as anode and Sn acts as cathode but when Fe contact with Zn, Fe acts as cathode where as Zn acts as anode.

PITTING CORROSION: Pitting corrosion is a localized and accelerated corrosion. When a small particles of dust or water etc are get deposited on a metal (like steel). The portion covered by the dust will not be well-aerated area compared to the exposed surface hence the covered surface becomes anodic with respect to the surface exposed. In presence of an conducting medium (moisture) corrosion starts below the dust part and forming a pit. Once pit is formed the ratio of corrosion increases, because of the formation of smaller anodic and larger cathodic area intense corrosion takes place.

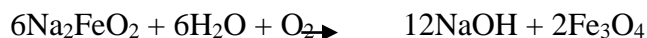
Pitting corrosion is one of the most destructive forms of corrosion. It causes equipment to fail because of perforation with only a small percent weight loss of the entire structure. Because of the small sizes of the pits it is highly difficult to identify the pitting corrosion. Pitting corrosion is an autocatalytic process, and once the corrosion products are formed, it further provides the condition for differential aeration below the corrosion product and surrounding metal parts. The pit grows and ultimately may cause failure of the metal.

Caustic embrittlement: It is a form of stress corrosion takes place in boilers operating at high temperature and pressure. Caustic embrittlement focus at stressed part of boilers such as cracks, rivets, bents, joints etc.

The boiler fed water usually contains some residual sodium carbonate (used for softening process). At high temperature and pressure it undergoes hydrolysis to form sodium hydroxide.



The alkali water sweeps through the minute cracks, crevices between the rivets and joints by capillary action. Inside the cracks water gets evaporated leaving behind NaOH. The concentrations of the NaOH gradually increase on these sites due to poor circulation of water. When concentrations of the NaOH reaches a value of 10% it attacks the metal at the stressed region dissolving it in the form of sodium ferroate (Na_2FeO_2). Sodium ferroate undergoes hydrolysis-depositing magnetite as follows



So NaOH is regenerated in the process and its concentration is keep on increasing maintaining a required environment. Thus corrosion process develops cracks and making the metal brittle by the deposition of the product.

The corrosion cell can be represented as

Fe (under stress) / conc. NaOH / dil. NaOH/ Fe (stress free)

Anode

Cathode

Caustic embrittlement can be prevented by the addition of compounds like sodium sulphite, tannin, lignin, phosphates etc. which blocks the cracks thereby preventing the infiltration of alkali.

Factors affecting rate of corrosion: Several factors affecting the rate of the corrosion, which can be divided into two parts

2. Factors affecting on metal (related to the metal)
3. Factors affecting on corrosive environment.

Factors affecting the metals:

1. **Nature of the metal:** The tendency of the metal to undergo corrosion is mainly dependent on the nature of the metal. IN general the metal with lower electrode potential have more reactive and more susceptible for corrosion and metal with high electrode potential are less reactive and less susceptible for corrosion for egs: metals like K, Na, Mg, Zn etc have low electrode potential are undergo corrosion very easily, where as noble metals like Ag, Au, Pt have higher electrode potential, their corrosion rate are negligible but there are few exception for this general trend as some metals show the property of passivity like Al, Cr, Ti, Ta etc.
2. **Surface state of the metal or nature of the corrosion product (passivity):**
The corrosion product is usually the oxide of the metal; the nature of the product determines the rate of further corrosion process.

If the oxide layer, which forms on the surface, is stoichiometric, highly insoluble and non-porous in nature with low ionic and electronic conductivity then that type of products

layer effectively prevents further corrosion, which acts as a protective film. For egs: Al, Cr, Ti develop such a layer on their surface and become passive to corrosion and some metal like Ta, Zr and Mo not only forms such a protective layers but are capable of self repairing oxide films when it is damaged. Hence these are extremely passive metals.

If the oxide layer forms on the metal surface is non-stoichiometric, soluble, unstable and porous in nature and have an appreciable conductivity, they cannot control corrosion on the metal surface for egs: oxide layer formed on metals like Zn, Fe, Mg etc.

3. Anodic and Cathodic area:

The rate of the corrosion is greatly influenced by the relative sizes of cathodic and anodic areas.

If the metal has smaller the anodic area and larger the cathodic area exposed to corrosive atmosphere, more intense and faster is the corrosion occurring at anodic area because at anode oxidation takes place and electrons are liberated. At the cathode these electrons are consumed. When anode is smaller and cathode region is larger all the liberated electrons at anode are rapidly consumed. This process makes the anodic reaction to takes place at its maximum rate thus increasing the corrosion rate. If the cathode is smaller and reverse process takes place decrease rate of corrosion.

For egs: If tin (Sn) coated on iron (Fe) and in that some area are not covered or some pin holes are left, there forms smaller anodic area and larger cathodic area because tin is cathodic with respect to iron so intense localized corrosion takes place. On the other hand if Zn coated to Fe then if there are some pin holes are there creates larger anodic area and smaller cathodic area because Fe is cathodic with respect to zinc so that rate of corrosion is very less.

4. Hydrogen over voltage:

A metal with low hydrogen over voltage on its surface is more susceptible for corrosion. When the cathodic reaction is hydrogen evolution type with low hydrogen over voltage, liberation of H_2 gas is easier so that cathodic reaction is very fast, that makes anodic reaction faster hence overall corrosion process is very fast. If the H_2 over voltage is high so cathodic reaction is slow hence corrosion reaction also slower.

Factors related to corrosive environment:

1. **pH of the medium:** Usually higher acidic nature (low pH) higher is the rate of corrosion. If the pH is greater than 10 corrosion of iron is very less due to the formation of protective coating of hydrous oxides of iron.
If pH is between 10 and 3, then presence of oxygen is essential for corrosion of iron. If the pH is 3 or lower than 3, severe corrosion occurs in the absence of air due to the continuous evolution of H_2 at cathode. However metals like Al, Zn etc undergo fast corrosion in highly alkaline medium.
2. **Temperature:** On increasing the temp. Rate of corrosion process also gets increases because on increase of temp. Conductance of the aqueous medium increases hence rate of diffusion also.
In some cases on rise in temp. Decrease the passivity, which again leads to increase in the corrosion rate.
3. **Polarization at anodic and cathodic area:** Polarization of cathode or anode decreases the rate of corrosion. If anodic polarization takes place due to some reaction, then tendency of metal to undergo oxidation decreases hence dissolution of metals as metal ion decreases. This is usually due to increase in conc. Of ions of the dissolved metals in the vicinity of electrode or also due to the anodic passivity. Cathode polarization decreases the cathodic reaction hence hindering the combination of cathode reactant and electron. For the corrosion to continue both anodic and cathodic reaction should take place simultaneously if any one reaction is slower than the rate of corrosion is slower. Use of depolarizers reduces the polarization effect hence the rate of corrosion reaction increases.

Galvanic corrosion or Corrosion of Metals due to contact of metals:

The name of this type of corrosion is indicative that there must be a formation of galvanic cell on metal surface causing corrosion. Such cells get set up all along the surface of metal when it faces the electrolytic environment and two dissimilar metals in contact.

For example:

- If metal iron or brass alloy is used together to join various parts, due to difference in potential, a galvanic cells gets set, leading to corrosion.
- In such cases all along the surface of metal small galvanic cells are set up, where area of high potential acts as an anode and the one with lower potential act as a cathode. The portion of metal acting as an anode deteriorates and at cathode the cathodic product gets evolved/deposited, depending upon the environment, and mechanism of the corrosion, i.e. by absorption of oxygen or evolution of hydrogen.
- When metals are surrounded by aqueous alkaline/acidic/neutral solution, the movement electrons, cations and anions occurs just like as in a typical galvanic cell. But when the

metal is just exposed to moisture or a few drops of certain solution, the movement of electrons, cations and anions takes place through the bulk of metal, thus the metal itself serves as a conducting medium while its outer surface gets corroded.

- If the metal is exposed to acidic medium the mechanism at cathode proceeds to form H_2 gas while anodic reactions remain the same.

Control of corrosion: *To avoid the formation of galvanic cells,*

- (a) The metals should be pure.
- (b) The materials used to assemble the different parts should be of same potentials.





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