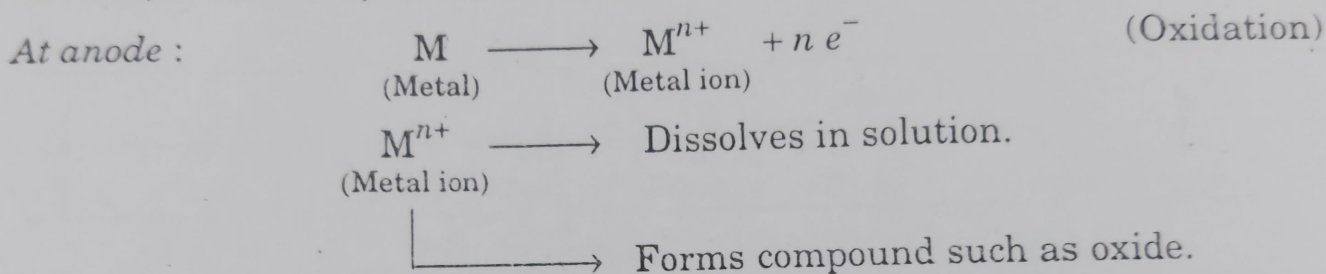


## II. Wet or Electrochemical Corrosion : Mechanism

### 6.3 WET OR ELECTROCHEMICAL CORROSION

This type of corrosion occurs : (i) where a conducting liquid is in contact with metal or (ii) when two dissimilar metals or alloys are either immersed or dipped partially in a solution. This corrosion occurs, due to the existence of separate 'anodic' and 'cathodic' areas/parts, between which current flows through the conducting solution. At **anodic area**, oxidation reaction (i.e., liberation of free electrons) takes place, so anodic metal is **destroyed** by either dissolving or assuming combined state (such as oxide, etc.) **Hence, corrosion always occurs at anodic areas.**



On the other hand, at **cathodic areas**, reduction reaction (i.e., gain of electrons) takes place. Usually, cathode reactions **do not** affect the cathode, since most metals cannot be further reduced. So at cathodic part, dissolved constituents in the conducting medium accept the electrons to form some ions (like  $\text{OH}^{-}$ ,  $\text{O}^{2-}$ ).

The metallic ions (at anodic part) and non-metallic ions (formed at cathodic part) diffuse towards each other through conducting medium and form a corrosion product **somewhere between anode and cathode**. The electrons set free at the anode flow through the metal and are finally consumed in the cathodic reaction. Thus, we may sum up that electrochemical corrosion involves : (i) the formation of anodic and cathodic areas or parts in contact with each other, (ii) presence of a conducting medium, (iii) corrosion of anodic areas only, and (iv) formation of corrosion product somewhere between anodic and cathodic areas.

## MECHANISM

### 6.4 MECHANISM OF WET OR ELECTROCHEMICAL CORROSION

**Electrochemical corrosion** involves flow of electron-current between the anodic and cathodic areas. The anodic reaction (i.e., at anodic area) involves in dissolution of metal as corresponding metallic ions with the liberation of free electrons.

At anodic area : 
$$M \longrightarrow M^{n+} + n e^{-} \quad (\text{Oxidation})$$

On the other hand, the cathodic reaction consumes electrons with either by: (i) evolution of hydrogen or (ii) absorption of oxygen, depending on the nature of the corrosive environment.

(a) **Evolution of hydrogen-type** corrosion occurs, usually, in **acidic environments**. Considering metal like Fe, the anodic reaction is dissolution of iron as ferrous ions with the liberation of electrons.

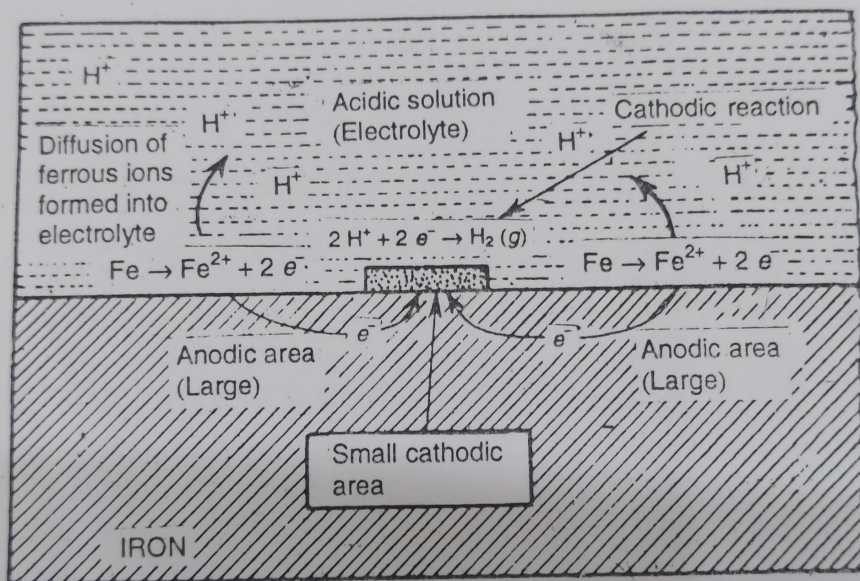
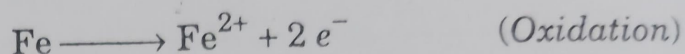
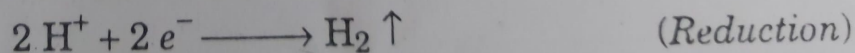


Fig. 6. Mechanism of wet corrosion by hydrogen evolution.

These electrons flow through the metal, from anode to cathode, where  $H^{+}$  ions (of acidic solution) are eliminated as hydrogen gas.



The overall reaction is : 
$$Fe + 2 H^{+} \longrightarrow Fe^{2+} + H_2 \uparrow$$

Thus, this type of corrosion causes "displacement of hydrogen ions from the acidic solution by metal ions." Consequently, all metals **above hydrogen** in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen.

**Note :** It may be pointed here that in hydrogen evolution-type of corrosion, the anodes are, usually *very large* areas ; whereas the cathodes are *small* areas.

(b) **Absorption of oxygen : Rusting of iron in neutral aqueous solution** of electrolytes (like NaCl solution) in the presence of atmospheric oxygen is a common



example of this type of corrosion. The surface of iron is, usually, coated with a thin film of iron oxide. However, if this iron oxide film develops some cracks, anodic areas are created on the surface; while the well-metal parts act as cathodes. It follows that the anodic areas are **small** surface parts; while nearly the rest of the surface of the metal forms **large** cathodes.

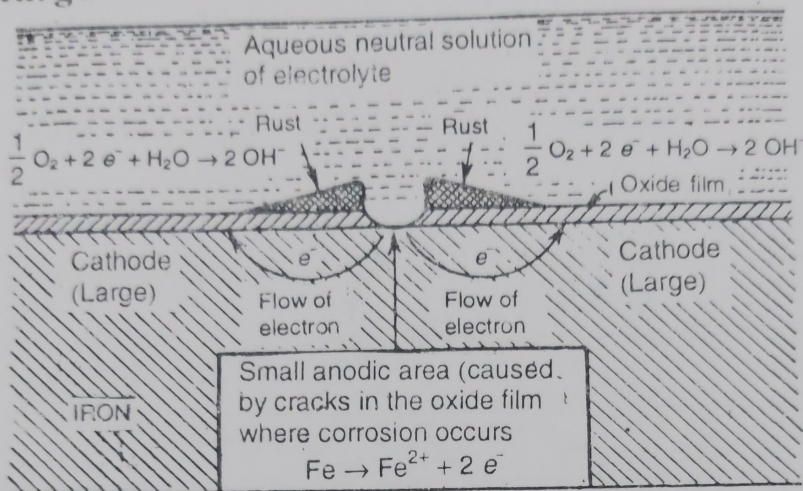
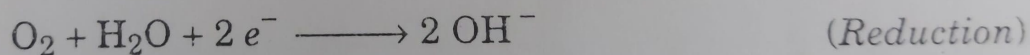


Fig. 7. Mechanism of wet corrosion by oxygen absorption.

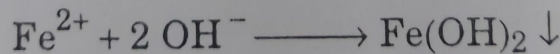
At the **anodic areas** of the metal (iron) dissolves as ferrous ions with liberation of electrons.



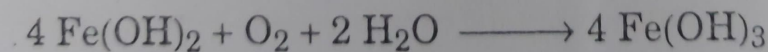
The liberated electrons flow from anodic to cathodic areas, through iron metal, where electrons are intercepted by the dissolved oxygen as:



The  $\text{Fe}^{2+}$  ions (at anode) and  $\text{OH}^-$  ions (at cathode) diffuse and when they meet, ferrous hydroxide is precipitated.



(i) If enough oxygen is present, ferrous hydroxide is easily oxidised to ferric hydroxide.



This product, called **yellow rust**, actually corresponds to  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ .

(ii) If the supply of oxygen is **limited**, the corrosion product may be even **black** anhydrous magnetite,  $\text{Fe}_3\text{O}_4$ .