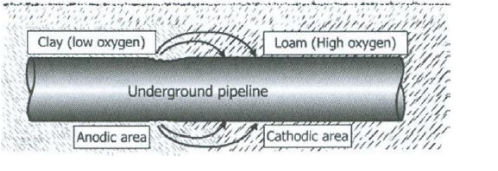
**Concentration Cells :**

This is similar to galvanic cells except the anode and cathode are of same metals in a heterogeneous electrolyte. A pipe in soil, Concentration cells may be set up by: (a) Variation in the amount of oxygen in soils. (b) Differences in moisture content of soils. (c) Differences in compositions of the soil. Concentration cells are commonly observed in underground corroding structures, such as buried pipes or tanks.



There are three general types of concentration cell corrosion:

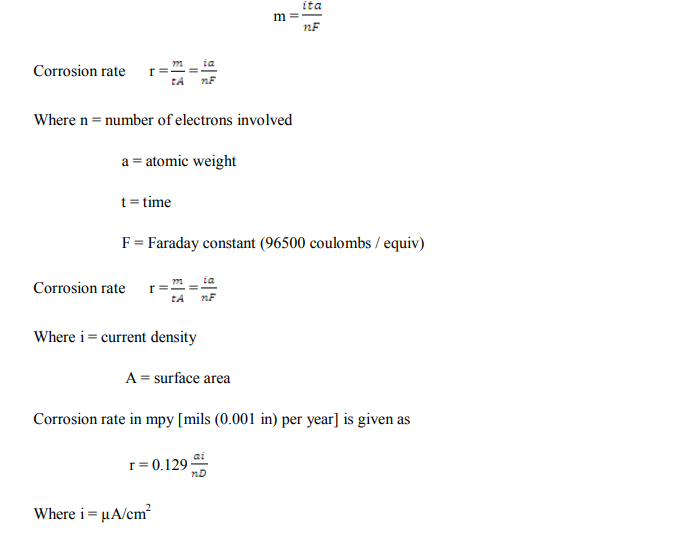
**1)**Metal Ion Concentration Cells In the presence of water, a high concentration of metal ions will exist under faying surfaces and a low concentration of metal ions will exist adjacent to the crevice created by the faying surfaces. An electrical potential will exist between the two points. The area of the metal in contact with the low concentration of metal ions will be cathodic and will be protected, and the area of metal in contact with the high metal ion concentration will be anodic and corroded.

**2)**Oxygen Concentration Cells A water solution in contact with the metal surface will normally contain dissolved oxygen. An oxygen cell can develop at any point where the oxygen in the air is not allowed to diffuse uniformly into the solution, thereby creating a difference in oxygen concentration between two points. Corrosion will occur at the area of low-oxygen concentration (anode).

**3)**Active-Passive Cells Metals that depend on a tightly adhering passive film (usually an oxide) for corrosion protection; e.g., austenitic corrosion-resistant steel, can be corroded by active-passive cells. The corrosive action usually starts as an oxygen concentration cell; e.g., salt deposits on the metal surface in the presence of water containing oxygen can create the oxygen cell. The inequality of dissolved chemicals causes a potential difference, which establishes anode in the more concentrated region and cathode in the less concentrated region.

**Electrode-Solution Interface – Definition and Types of Polarization**

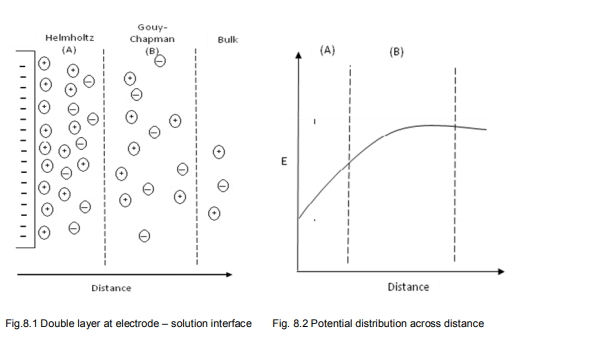
Proportionality between current density (i) and reacted mass (m) in an electrochemical reaction is stated by Faraday’s law.

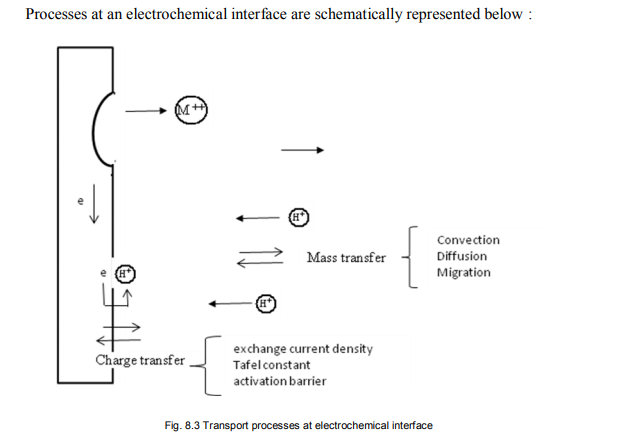


D = density, g/cm3

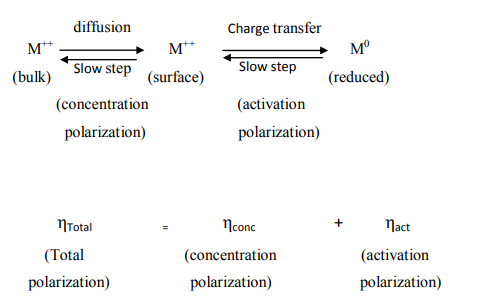
Through above relationship, anodic current density in corrosion can be converted to metal loss in mpy. When electrode reactions take place, the potential will no longer be at equilibrium due to current flow through an electrochemical cell-causing a change in the electrode potential. This electrochemical phenomenon is termed POLARIZATION. Polarization of anode – anodic polarization Polarization of cathode – cathodic polarization Corroding systems are not in equilibrium-deviation from thermodynamics. Deviation of the potential from its reversible value is referred to as polarization. A cell or electrode is said to be polarised when there is little or no change in current with larger changes in potential. An electrode is not in equilibrium when a net current flow from or to its surface. Polarization can result from either a slow step in an electrode process or discharge of ions at an electrode surface. Distribution of anions and cations at a metal – solution interface is shown as electrical double layer (Fig. 8.1).

A compact layer (Helmholtz) closest to metal surface in which charge distribution and hence potential varies linearly with distance (Fig. 8.2). A more diffuse innter layer (G. C. layer) where potential changes exponentially.





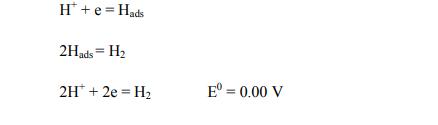
Mass transport to metal surface involves forces such as convection, diffusion and migration, depending on presence or absence of electric field and flow conditions. Concentration polarization is controlled by diffusion gradients (Fick’s law). Activation polarization involves kinetic factors related to charge transfer, such as activation energy barrier and equilibrium current density. Transport processes at an electrode – electrolyte interface are illustrated in Fig. 8.3. Consider a solid-solution interface. Diffusion of electro-active ions from bulk to the interface and interaction at electrode resulting from charge transfer.



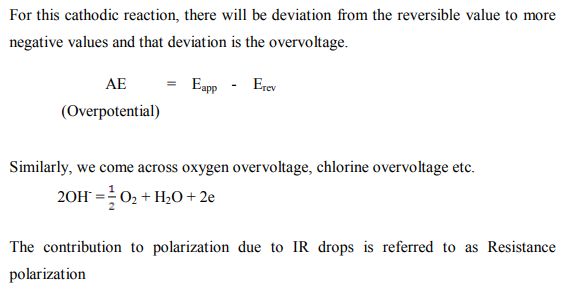
Polarization resulting from concentration gradients is termed concentration polarization; while activation polarization is caused by a slow step in the electrode reaction (electrode reaction requires activation energy in order to reach the final state)

Examples of activation polarization include:

Hydrogen overvoltage (overpotential)



For this cathodic reaction, there will be deviation from the reversible value to more negative values and that deviation is the overvoltage.



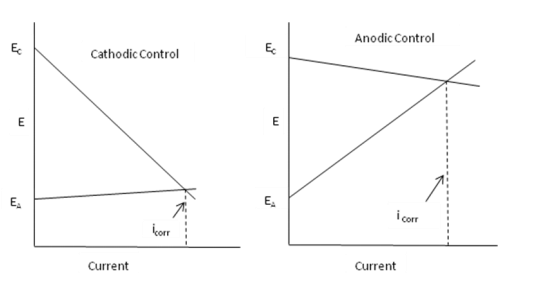
So Total polarization ηT = ηAct + ηConc + ηresist

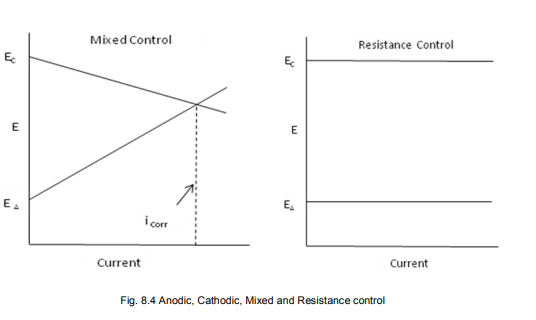
When polarization occurs mostly at anodes, corrosion reaction is Anodically

**Controlled** - Anodic process at electrode is accelerated by moving the potential in the positive direction.

When polarization occurs mostly at cathodes, it is Cathodically controlled - Cathodic process accelerated by moving the potential in the negative direction.

Resistance control when electrolyte / electrode resistance is so high that the current is insufficient to polarise either of the electrodes.





Mixed control refers to the condition where both anode and cathode are polarized. Schematic illustrations of anodic, cathodic, mixed and resistance controls are given in Fig 8.4.