CHAPTER 6
Modern Theory Principles

LECTURER
SAHEB M. MAHDI

Modern Theory principles in Corrosion and their applications :-

Corrosion studies can be carried-out by two methods

1 – Thermodynamics . or
2 – By electrode Kinetics .

Thermodynamics give the change in energy state , also predicts the directions of a reactions. For spontaneous reactions , the systems must decrease their Free-energy and move to a lower energy state, e.g. Corrosion is a spontaneous reaction. For non-spontaneous reactions energy must be added to the system in order to facilitate the reaction .

$Fe \rightarrow Fe_2O_3$ spontaneous ($-\Delta G$)
$Fe \leftarrow Fe_2O_3$ Non-spontaneous ($+\Delta G$)

By thermodynamic rate of reaction can not be predicted.
Free Energy: Driving Force of a Chemical Reaction

$Mg+H_2O(l)+\frac{1}{2}O(g) \rightarrow Mg(OH)_2(s)$ …… $\Delta G^o = -596{,}600J$ Spontaneous

$Cu+H_2O(l)+\frac{1}{2}O(g) \rightarrow Cu(OH)_2(s)$ …… $\Delta G^o = -119{,}700J$ Spontaneous

$Au+3/2H_2O(l)+3/4O(g) \rightarrow Au(OH)_3(s)$ …… $\Delta G^o = +65{,}700J$ Non-Spontaneous

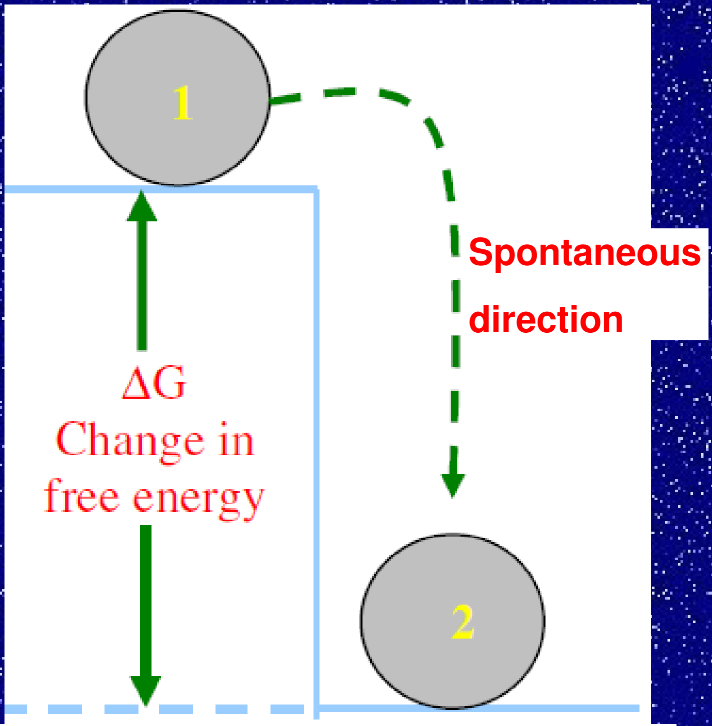


Fig.(1) mechanical analogy of free energy change.

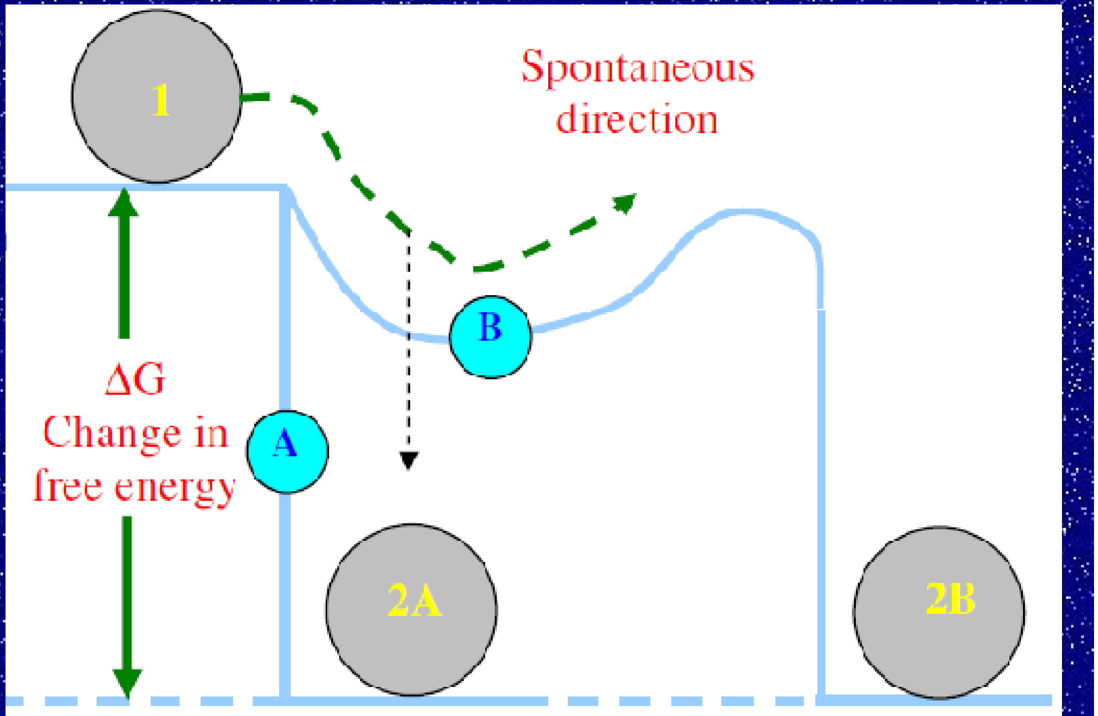
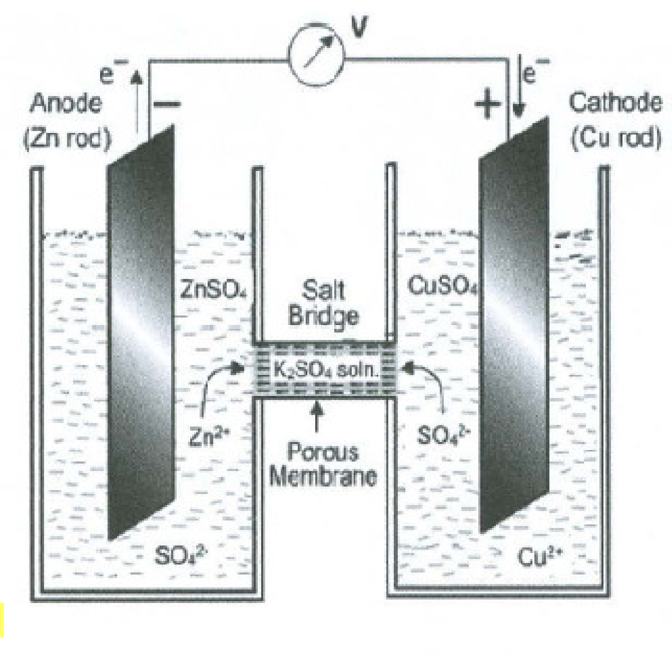


Fig.(2) Effect of reaction path on reaction rate.

Change in free-energy under equilibrium conditions is given as :

$$\Delta G = -EnF$$

ΔG is in Joules
E is emf in volts
n is the number of electrons involved in the reaction
F is the Faraday (96500 C/equivalent)



For the Zn/ $ZnSO_4$ half cell and Cu/$CuSO_4$ half cell , Zn^{+2} & Cu^{+2} Are in unit activity. A unit activity, Means 1gram atom of element salt (Zn salt ; Cu salt) / 1 liter of Aqueous solution (electrolyte).

As long as the Zn and Cu electrodes are not connected (short-circuited). There is no flow of current .But theoretically electro-chemical reactions are occurs at individual electrodes, e.g.

$Zn \rightarrow Zn^{+2} + 2e$
$Zn^{+2} + 2e \rightarrow Zn$ **and**

$Cu \rightarrow Cu^{+2} + 2e$
$Cu^{+2} + 2e \rightarrow Cu$

If the Oxidant and Reducing species are at unit activity , then cell potential is calculated by Nerst equation . for Cu potential

$$E = E^{o} + 2.3 \frac{R\,T}{n\,F} \log \frac{a(\mathrm{oxid.})}{a(red.)}$$

E – standard cell potential vs. SHE .
R – gas constant (8.3 J/Ko/mole).
T – temperature (Ko).
n – electron involves (Valence).
F – faraday constant (96,500 coulomb).
a(oxid.) – concentration of oxidizing species / liter .
a(red.) – concentration of reducing species / liter .

The change in free energy gives an idea of content of energy displacement .But it dose not give the velocity or the rate of electro-chemical reaction. The other limitation equilibrium states, which are difficult to establish in corrosion reactions.

Free energy calculation have been used to determine :-

1 – Spontaneous direction of a reaction .
2 – Estimating the composition of corrosion products.
3 – Predicting the environment changes that will reduce the corrosion rate.

2 & 3 could be explained by the potential vs. pH diagram of a metal (also called pourbaix diagrams) . e.g. iron in water .

Redox potential or e.m.f. series is a thermodynamic function – redox has been utilized to predict the corrosivity of metals in various environments. e.g. metals (-ve) to hydrogen electrode would corrodes in acids but metals (+ve) to hydrogen electrode would not corrode in the absence of oxygen.

(-ve) such as (Fe or Zn) + Acid → Corrosion
(+ve) such as (Cu or Ag) + Acid → no corrosion
(Cu or Ag) + Acid + O_2 → Corrosion would happen in this case .
$Cu + H_2SO_4 \rightarrow$ No corrosion (Cu/Cu^{+2} more + than H_2/ H^+)
$Cu + H_2SO_4 + O_2 \rightarrow 2CuSO_4 + 2H_2O$ (O_2/ H_2O more + than Cu/Cu^{+2})

The corrosion rate of a metal decrease in presence of Oxygen in acids. With the increase in electro-positive character of a metal (e.g. Pt , Pb , …..etc) are un-affected by containing O_2 .

Pourbaix Diagram:-

1) Marcel Pourbaix developed potential-pH diagrams to show the thermodynamic state of most metals in dilute aqueous solutions
2) With pH as abscissa and potential as ordinate, these diagrams have curves representing chemical and electrochemical equilibria between metal and aqueous environment
3) These diagrams ultimately show the conditions for immunity, corrosion or passivation.

Equilibrium Reactions of iron in Water

$2\,e^- + 2H^+ = H_2$

$4\,e^- + O_2 + 4H^+ = 2H_2O$

$2\,e^- + Fe(OH)_2 + 2H^+ = Fe + 2H_2O$

$2\,e^- + Fe^{2+} = Fe$

$2\,e^- + Fe(OH)^{3-} + 3H^+ = Fe + 3H_2O$

$e^- + Fe(OH)_3 + H^+ = Fe(OH)_2 + H_2O$

$e^- + Fe(OH)_3 + 3H^+ = Fe^{2+} + 3H_2O$

$Fe(OH)^{3-} + H^+ = Fe(OH)_2 + H_2O$

$e^- + Fe(OH)_3 = Fe(OH)^{3-}$

$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H_+$

$Fe^{2+} + 2H_2O = Fe(OH)_2 + 2H^+$

$e^- + Fe^{3+} = Fe^{2+}$

$Fe^{2+} + H_2O = FeOH^+ + H^+$

$FeOH^+ + H_2O = Fe(OH)_2(sln) + H^+$

$Fe(OH)_2(sln) + H_2O = Fe(OH)^{3-} + H^+$

$Fe^{3+} + H2O = FeOH^{2+} + H^+$

$FeOH^{2+} + H_2O = Fe(OH)^{2+} + H^+$

$Fe(OH)^{2+} + H_2O = Fe(OH)_3(sln) + H^+$

$FeOH^{2+} + H^+ = Fe^{2+} + H_2O$

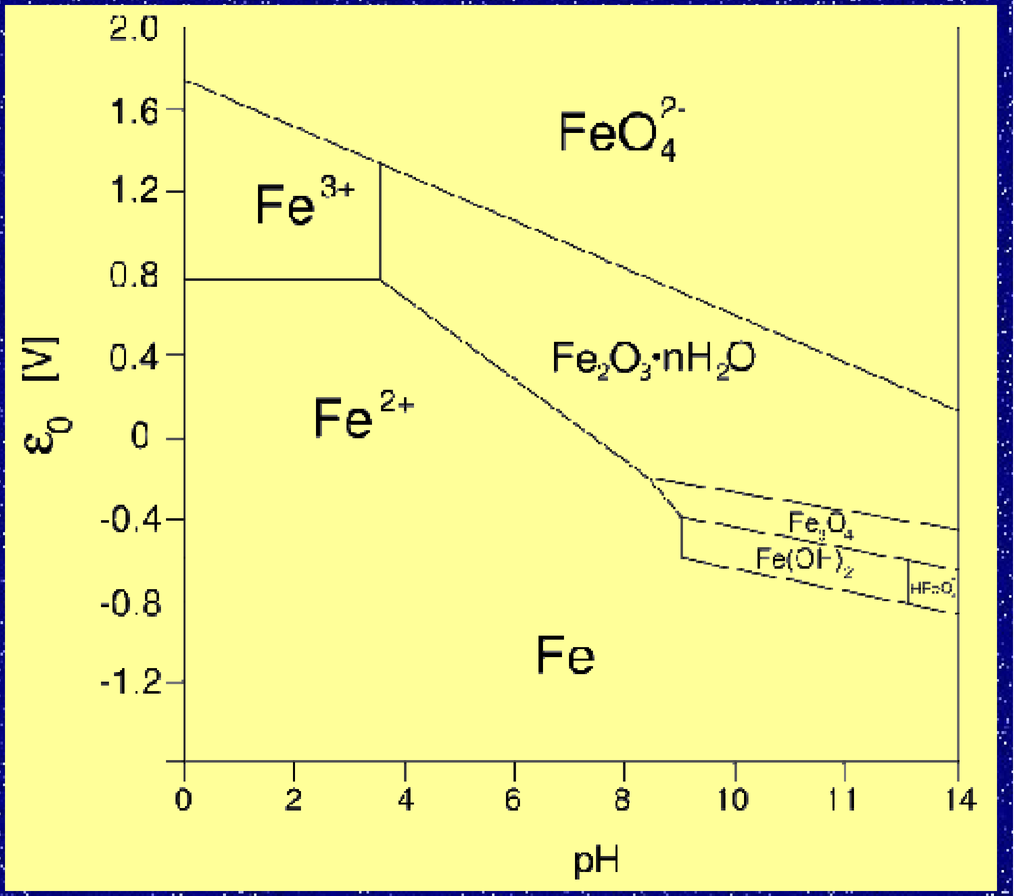
$e^- + Fe(OH)^{2+} + 2H^+ = Fe^{2+} + 2H_2O$

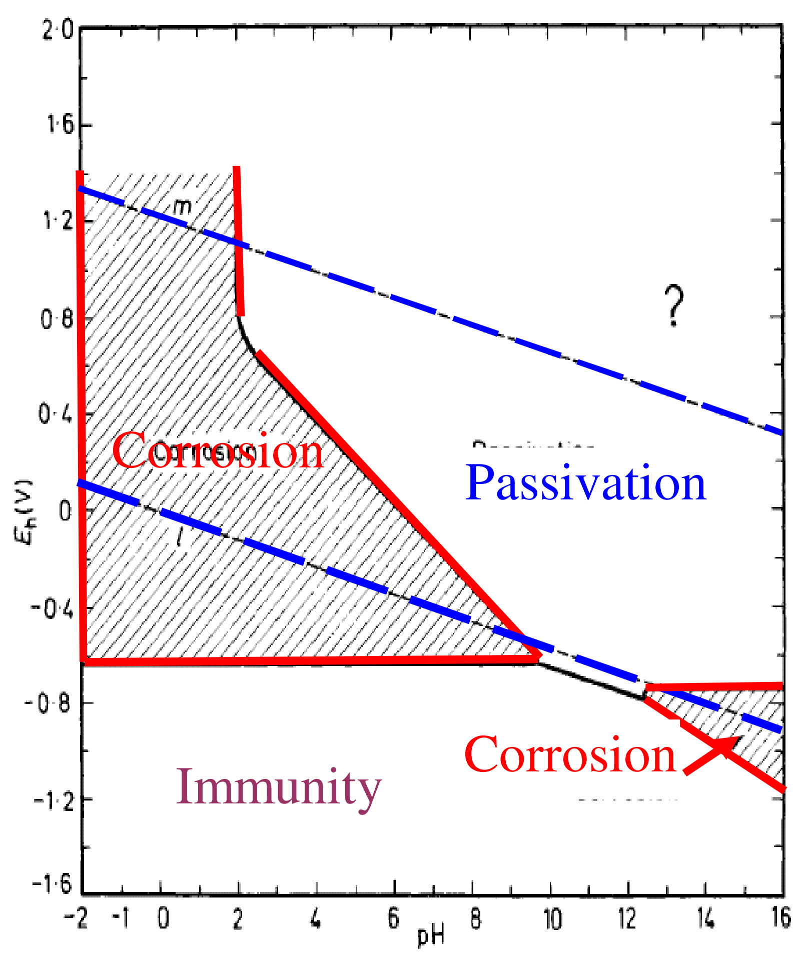
$e^- + Fe(OH)_3(sln) + H^+ = Fe(OH)_2(sln) + H_2O$

$e^- + Fe(OH)_3(sln) + 2H^+ = FeOH^+ + 2H_2O$

$e^- + Fe(OH)_3(sln) + 3H^+ = Fe^{2+} + 3H_2O$

Pourbaix Diagram for Iron





Benefits of Pourbaix Diagram

1 -Pourbaix diagrams offer a large volume of thermodynamic information in a very efficient and compact format.

2 -The information in the diagrams can be beneficially used to control corrosion of pure metals in the aqueous environment.

- By altering the pH and potential to the regions of immunity and passivation, corrosion can be controlled. For example, on increasing the pH of environment in moving to slightly alkaline regions, the corrosion of iron can be controlled.
- Changing the potential of iron to more negative values eliminate corrosion, this technique is called Cathodic protection.
- Raising the potentials to more positive values reduces the corrosion by formation of stable films of oxides on the surface of transition metals.

Limitations of Pourbaix Diagrams

1)These diagrams are purely based on thermodynamic data and do not provide any information on the reaction rates.

2)Consideration is given only to equilibrium conditions in specified environment and factors, such as temperature and velocity are not considered which may seriously affect the corrosion rate

3)Pourbaix diagrams deal with pure metals which are not of much interest to the engineers

2-Electrode Kinetics :-

We are interested in what happens when cells such as shown in fig.(3). In this short-circuited cell , a vigorous reaction occurs .The zinc Electrode rapidly dissolves in the solution and simultaneously a rapid evolution of hydrogen is observed at platinum electrode. Electrons released from the Zn dissolution and consumed in the hydrogen-reduction reaction.

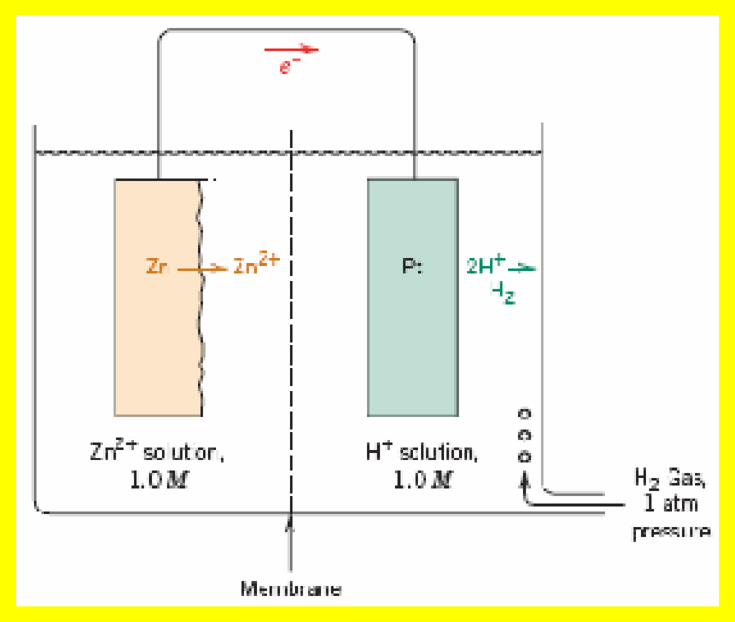


Fig.(3) Electrochemical cell consisting of standard Zn & Hydrogen electrodes that has been short-circuited

This process is the same of Fig.(4) ,In both the overall reaction is Zn dissolution and H_2 evolution .The potentials of these electrodes will no longer be at their equilibrium potential. This deviation from equilibrium potential is called *Polarization* (the displacement of electrode potential resulting from a net current). It is measured in terms of *overvoltage* (η) .The overvoltage is stated in terms of volts or mill volts plus or minus with respect to equilibrium potential (zero reference). From fig.(3) the potential after coupling is (- 0.66 V) .Its overvoltage is (+100mV or +0.10 V).

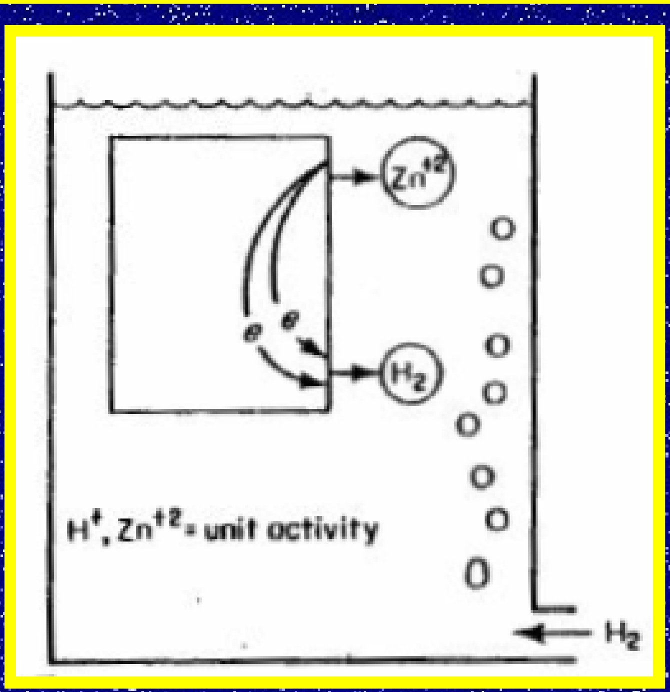


Fig.(4) Corroding Zn schematic.

Exchange Current Density :-

By plotting electrode potential versus reaction rate as shown in Fig.(5) ,it is possible to establish a point corresponding to the platinum-hydrogen electrode. This point represents the particular exchange reaction rate of electrode expressed in terms of moles reacting per square centimeter per second , no net reaction (oxidation rate = reduction rate = exchange reaction rate). Exchange reaction rate can be expressed in terms of current density , and current density can be directly derived from Faraday's law:

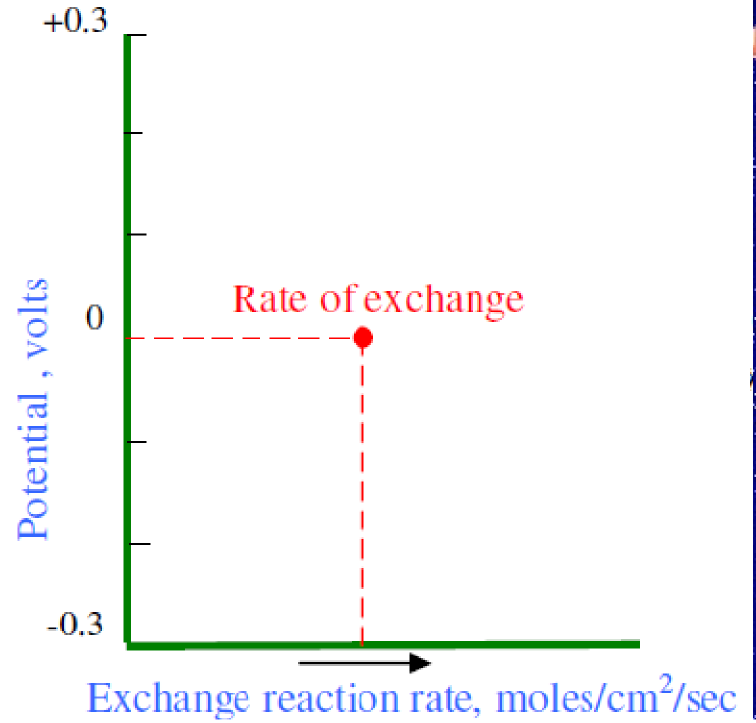


Fig.(5) Hydrogen-Hydrogen ion on Platinum.

$$r_{oxid} = r_{red} = \frac{i_o}{nF} \ldots\ldots\ldots (1)$$

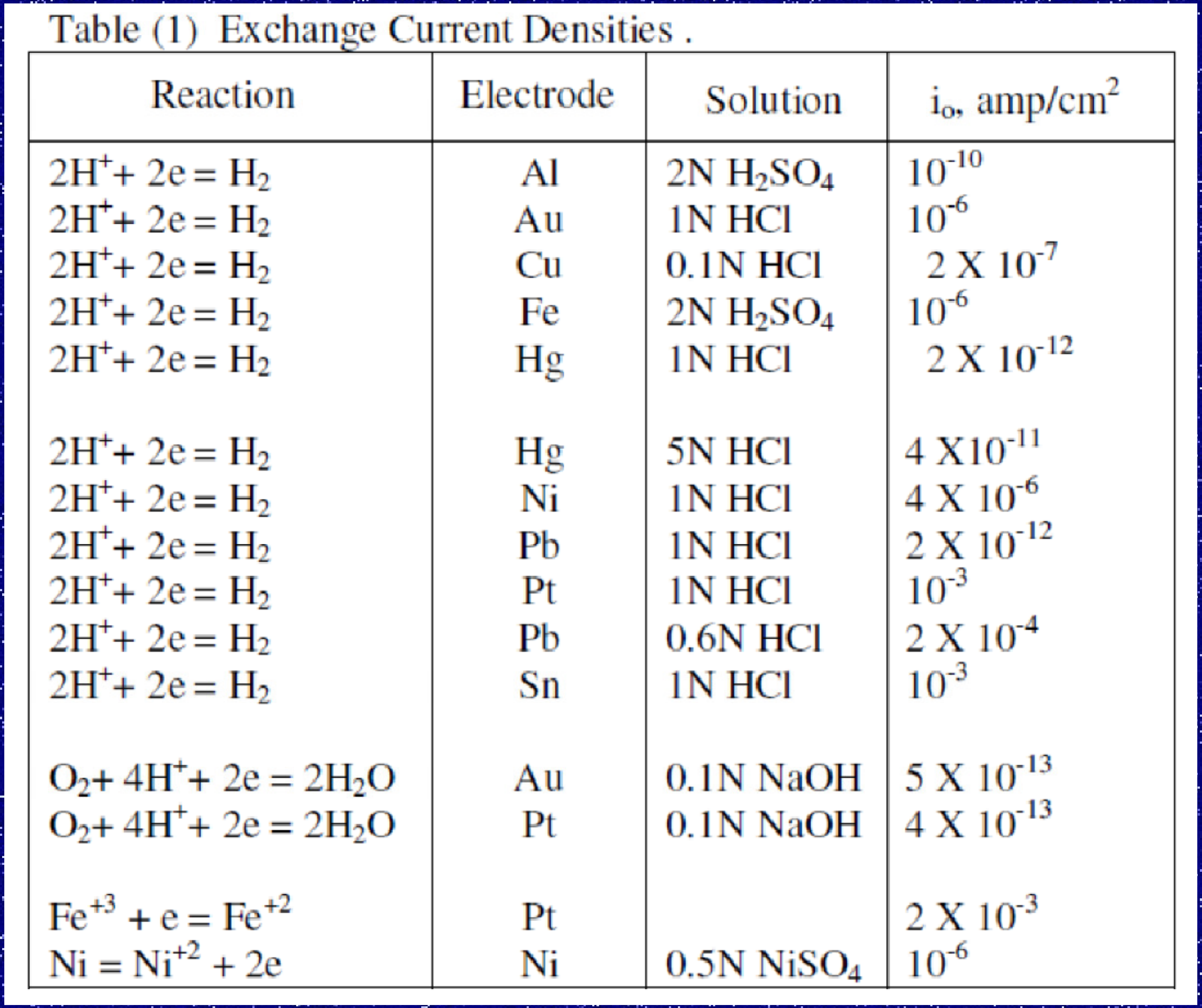


Table (1) Exchange Current Densities .

Reaction	Electrode	Solution	i_o, amp/cm^2
$2H^+ + 2e = H_2$	Al	2N H_2SO_4	10^{-10}
$2H^+ + 2e = H_2$	Au	1N HCl	10^{-6}
$2H^+ + 2e = H_2$	Cu	0.1N HCl	$2 X 10^{-7}$
$2H^+ + 2e = H_2$	Fe	2N H_2SO_4	10^{-6}
$2H^+ + 2e = H_2$	Hg	1N HCl	$2 X 10^{-12}$
$2H^+ + 2e = H_2$	Hg	5N HCl	$4 X 10^{-11}$
$2H^+ + 2e = H_2$	Ni	1N HCl	$4 X 10^{-6}$
$2H^+ + 2e = H_2$	Pb	1N HCl	$2 X 10^{-12}$
$2H^+ + 2e = H_2$	Pt	1N HCl	10^{-3}
$2H^+ + 2e = H_2$	Pb	0.6N HCl	$2 X 10^{-4}$
$2H^+ + 2e = H_2$	Sn	1N HCl	10^{-3}
$O_2 + 4H^+ + 2e = 2H_2O$	Au	0.1N NaOH	$5 X 10^{-13}$
$O_2 + 4H^+ + 2e = 2H_2O$	Pt	0.1N NaOH	$4 X 10^{-13}$
$Fe^{+3} + e = Fe^{+2}$	Pt		$2 X 10^{-3}$
$Ni = Ni^{+2} + 2e$	Ni	0.5N $NiSO_4$	10^{-6}

Exchange current density depends on :-

1) Redox potential of a metal.
2) Composition of electrode.
3) Temp. of the system.
4) The ratio of oxidized and reduced spacies.

Polarization :

Means the reduction in corrosion rate either by slowing down the anodic or Cathodic reaction.

Activation Polarization

refers to the condition wherein the reaction rate is controlled by the one step in the series that occurs at the slowest rate. The term “activation” is applied to this type of polarization because an activation energy barrier is associated with this slowest, rate-limiting step.

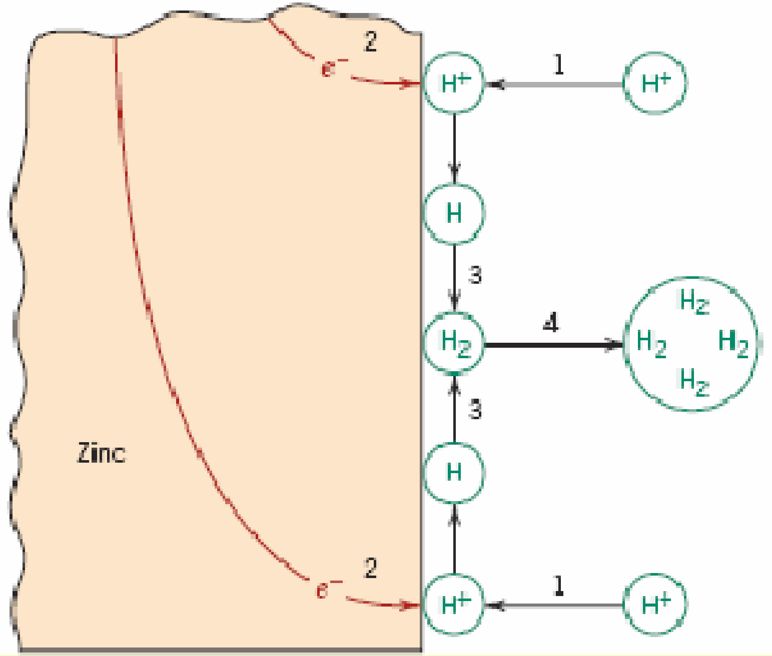


Fig.(6) representation of possible steps in hydrogen reduction. The rate of which is controlled by Activation polarization.

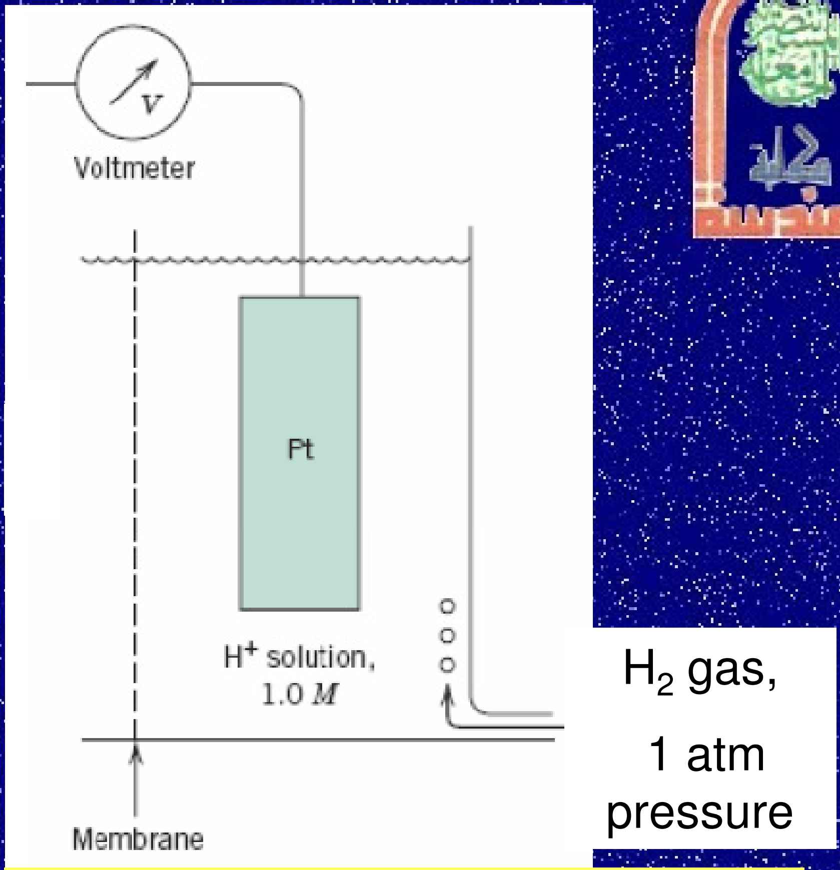


Fig.(7) The standard Hydrogen reference half-cell.

Considering the reduction of hydrogen ions to form bubbles of hydrogen gas on the surface of a zinc electrode.
The slowest of these steps determines the rate of the overall reaction.

For activation polarization, the relationship between overvoltage η_a and current density i is

$$\eta_a = \pm \log \frac{i}{i_o}$$

Called Tafel equation

Where β and i_o are constants for the particular half-cell. The parameter i_o is termed the *exchange current density,* which deserves a brief explanation. Equilibrium for some particular half-cell reaction is really a dynamic state on the atomic level. That is, oxidation and reduction processes are occurring, but both at the same rate, so that there is no net reaction. For example, for the standard hydrogen cell (Fig. 7) reduction of hydrogen ions in solution will take place at the surface of the platinum electrode according to

$$2H^+ + 2e \rightarrow H_2$$

With a corresponding rate $r_{red.}$ similarly, hydrogen gas in the solution will experience oxidation as

$$H2 \rightarrow 2H^+ + 2e$$

At rate $r_{oxid.}$ Equilibrium exists when $r_{red} = r_{oxid}$

This exchange current density is the current density from Equation (1) at equilibrium, or

$$r_{red} = r_{oxid} = \frac{i_o}{nF} \qquad ....(1)$$

Also Faraday's law can be written in terms of weight gain or loss

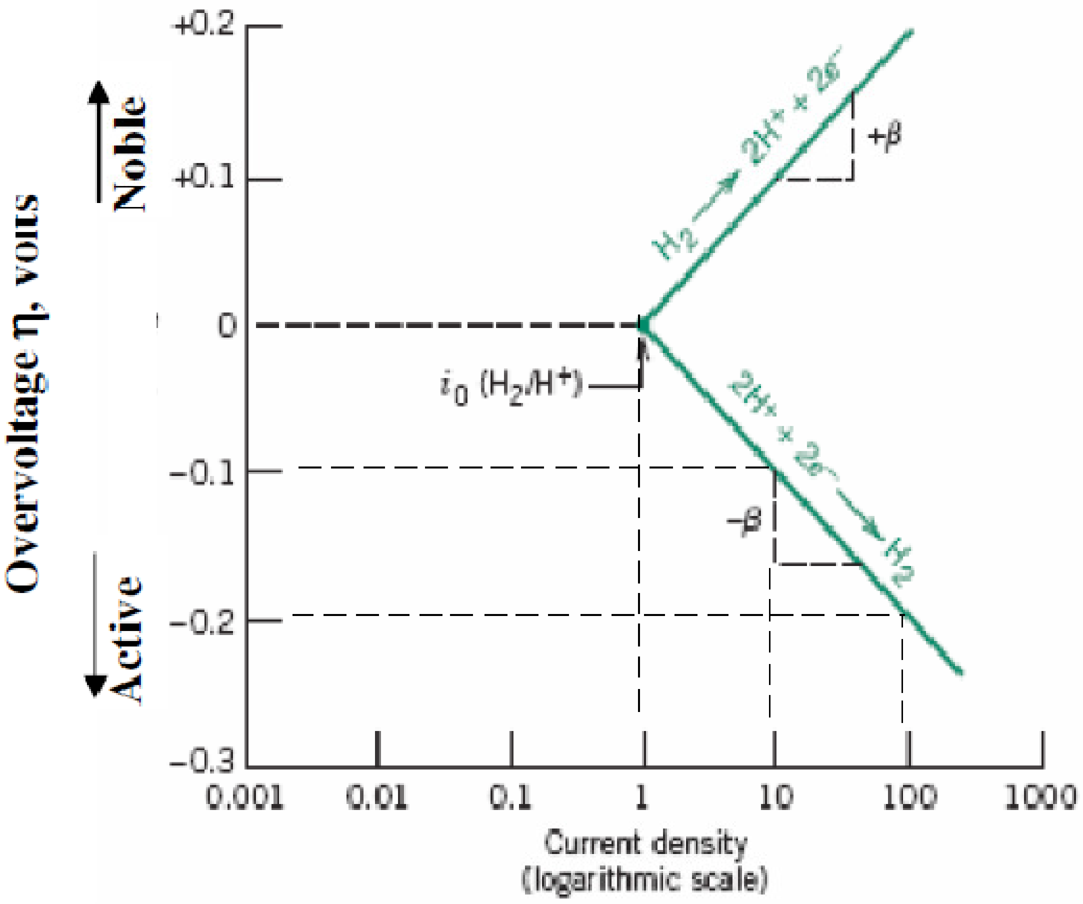
$$W = \frac{I\,t\,M}{n\,F} \quad \text{or} \quad W = \frac{i\,A\,t\,M}{n\,F}$$

(Very important equation)

Where W = Corrosion rate in weight gain or loss (gm).
i = exchange current density (A / cm^2).
t = exposure time (sec.)
M = Atomic weight of the metal (gm / mole).
n = No. of electrons transferred (the valence).
F = Faraday's constant (96,500 coulomb's or A.Sec./ mole).
I = Current (A).
A = Corroded surface area (cm^2)

Tafel equation is graphically illustrated in **Fig (8)** .If a logarithmic scale is used, the relationship between overvoltage or potential and current density is linear function. The value of the **(β slope or Tafel constant)** for electrochemical reactions ranges between **0.05 and 0.15 volt (in general β = 0.1 volt).**

Fig.(8) For a hydrogen electrode, Plot of activation polarization overvoltage versus logarithm of current and reduction reactions.



Both line segments originate at the exchange current density, and at zero overvoltage, since at this point the system is at equilibrium and there is no net reaction

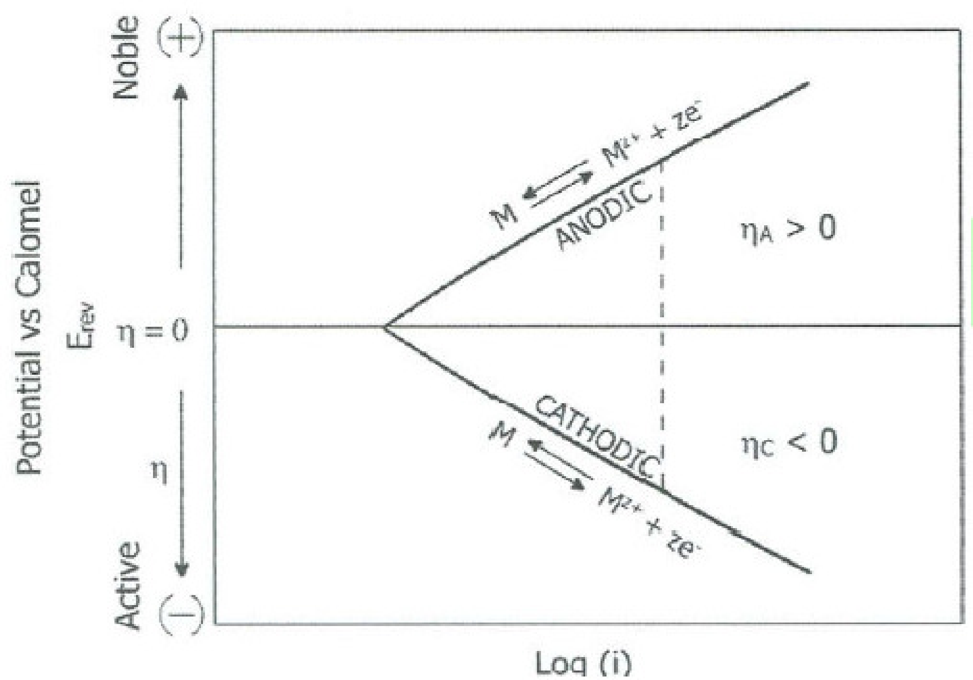


Fig.(8a) Polarization diagram.
(reversible electrode)

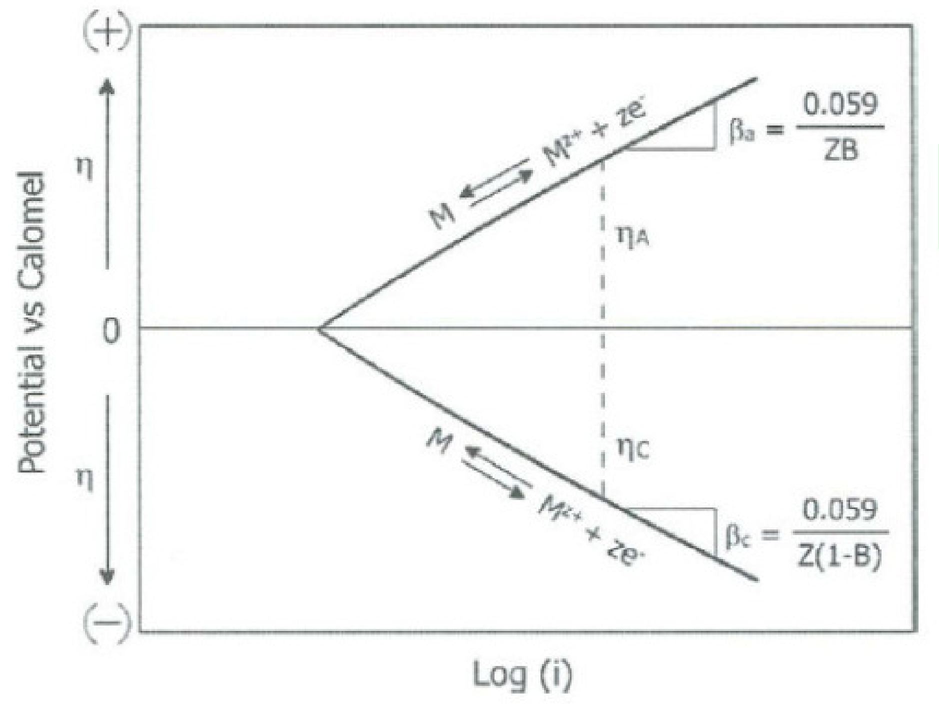


Fig.(8b) Polarization diagram of Zinc
in contact with its own ions.

Concentration Polarization

Concentration polarization exists when the reaction rate is limited by diffusion in the solution.

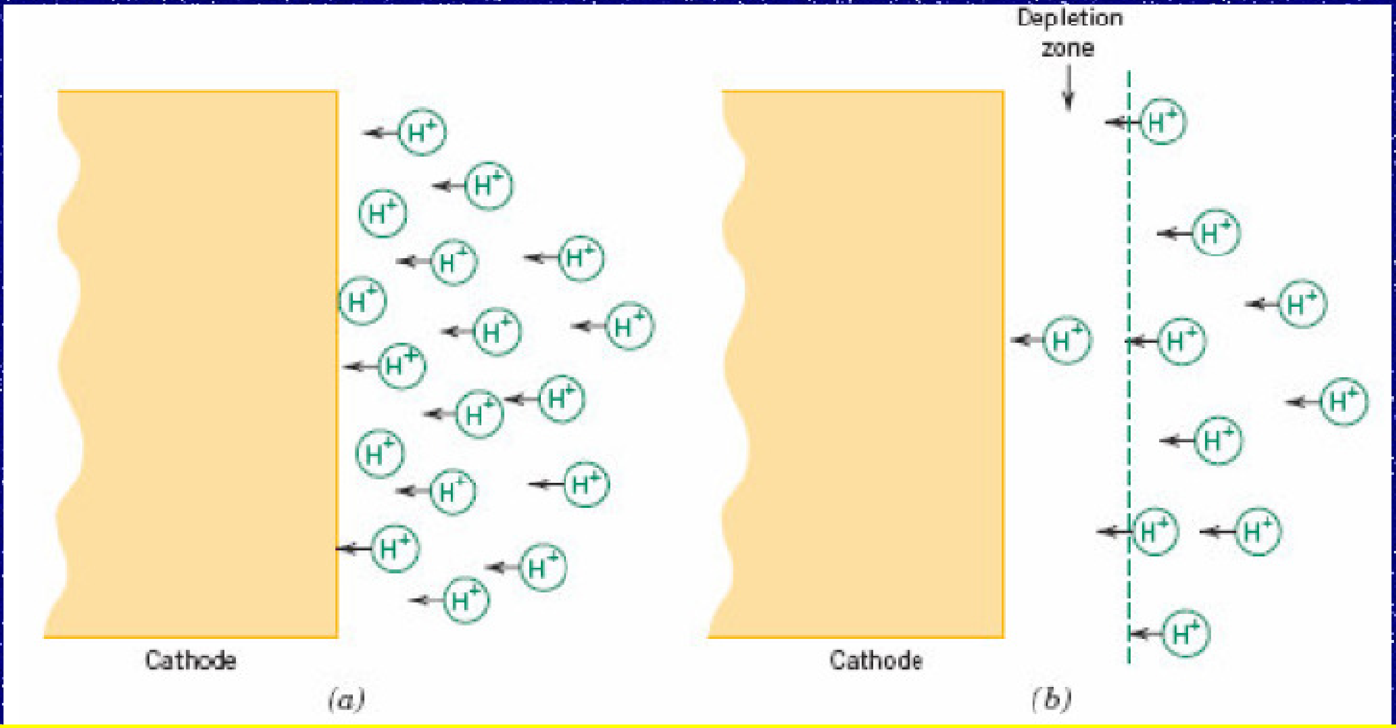


Fig.(9) For hydrogen reduction, schematic representation of the H^+ distribution in the vicinity of the cathode for (a) low reaction rates and/or high concentrations, and (b) high reaction rates and/or low concentration wherein a depletion zone is formed that gives rise to concentration polarization.

In concentration polarization we calculate the *limiting diffusion current density* iL .It represent the maximum rate of reduction possible for a given system; the eq. expressing this parameter is

$$i_L = \frac{D\,n\,F\,C_B}{X} \qquad \text{..........(2)}$$

Where iL = limiting diffusion current density .

D = diffusion coefficient of the reaction ions.

C = concentration of the reacting ions in the bulk solution.

X = thickness of the diffusion layer .

The diffusion-layer thickness is influenced by the *shape* of the particular electrode, the *geometry* of the system, and by *agitation*. If we consider no activation polarization , then the equation for concentration polarization is :

$$\eta_c = 2.3\frac{RT}{nF}\log\left(1-\frac{i}{i_l}\right) \qquad \text{..........(3)}$$

A graphical representation of the eq.(2) is shown in fig.(10).

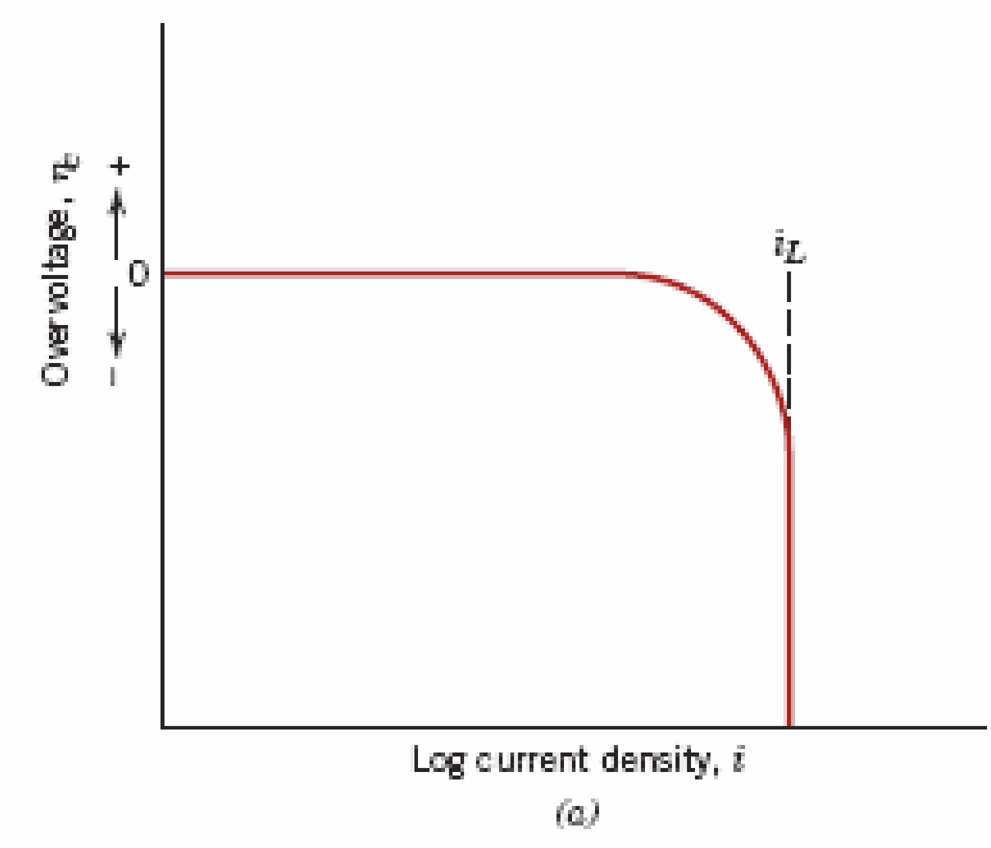


Fig.(10) For reduction reactions. Schematic plots of overvoltage versus logarithm of current density for Concentration polarization .

Fig. (11) illustrate the effects of changing limiting diffusion current on the shape of the polarization curve encountered during concentration polarization. As the solution velocity , concentration , or temperature are increased, limiting diffusion current increases since all of these factors exert an influence as indicated in eq.(2).

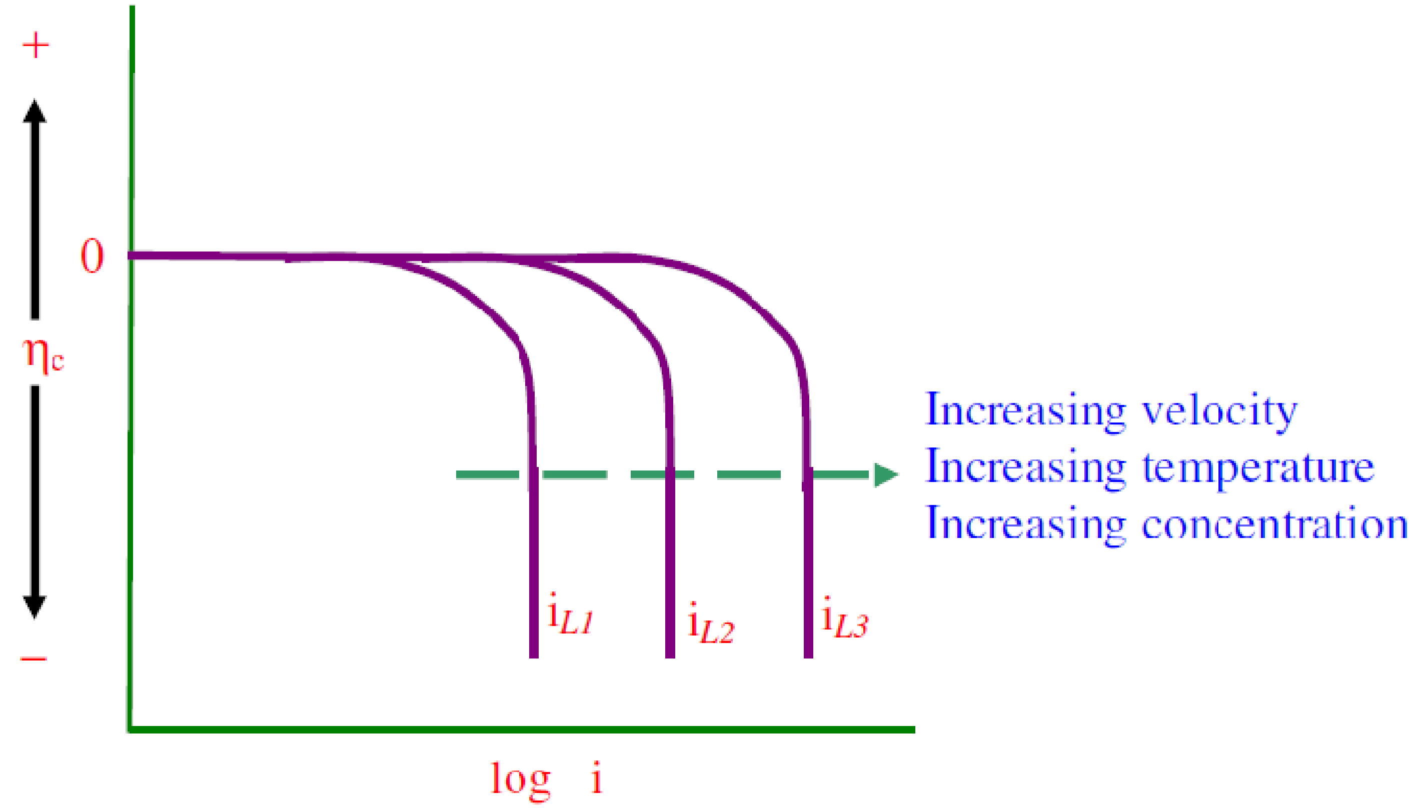


Fig.(11) Effect of environmental variables on concentration polarization curve.

Combined Polarization

Both activation and concentration polarization usually occur at an electrode. At low reaction rates, activation polarization usually controls, while at higher reaction rates concentration polarization becomes controlling. The total polarization of an electrode is the sum of the contributions of activation polarization and concentration polarization.

Corrosion Rates from Polarization Data

$$\eta_T = \eta_a + \eta_c$$

Equation for the kinetic of anodic dissolution is given by:

$$\eta_{\mathrm{diss}} = \beta \log \frac{\mathrm{i}}{\mathrm{i_o}}$$

$$\eta_{red} = -\beta \log \frac{\mathrm{i}}{\mathrm{i_o}} + 2.3 \frac{RT}{nF} \log \left(1 - \frac{i}{i_l} \right)$$

This equation is graphically illustrated in fig.(12).

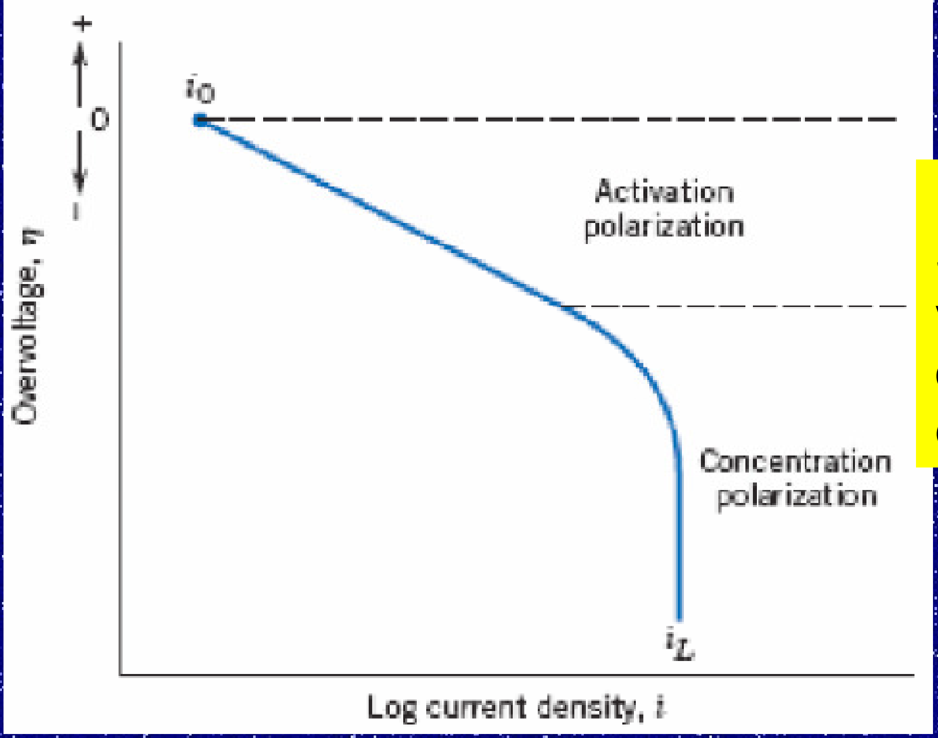


Fig.(12) For reduction reactions. Schematic plots of overvoltage versus logarithm of current density for combined activation-concentration polarization .

Mixed – potential Theory

The mixed – potential theory consist of two simple hypotheses:

1- Any electrochemical reaction can be divided into two or more partial oxidation and reduction reactions.

2- There can be no net accumulation of electrical charge during an electrochemical reaction.

During the corrosion of an electrically isolated metal sample, the total rate of oxidation must equal the total rate of reduction.

A mixed electrode is an electrode or metal sample which is in contact with two or more oxidation – reduction systems.

Example Zn immersed in HCl, such in Figure (13)

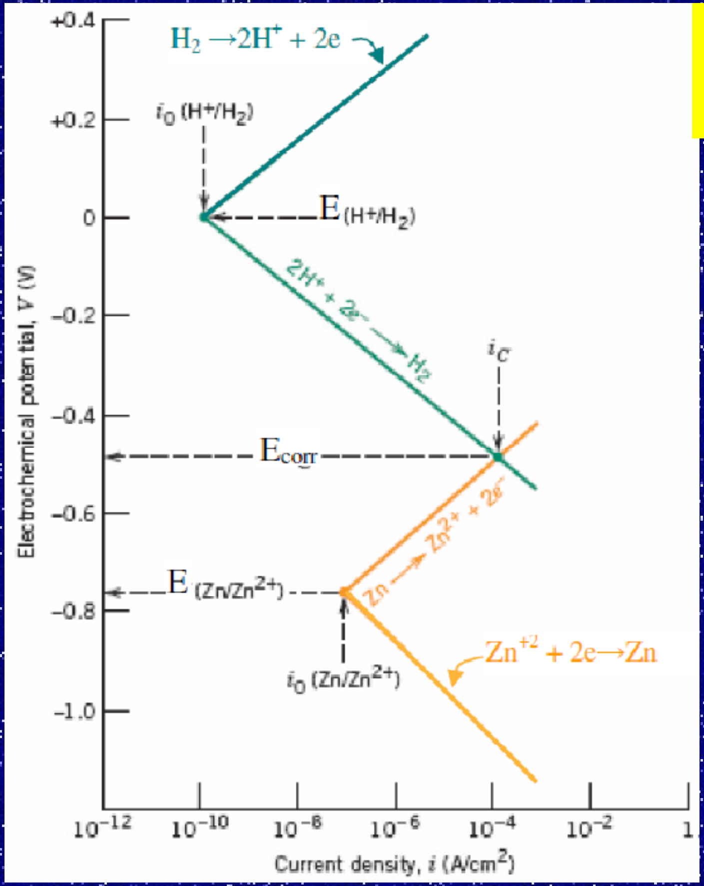


Fig.(13) Electrode kinetic behavior of zinc in an acid solution.

Both oxidation and reduction reactions are rate limited by activation polarization.

Corrosion behavior of Iron in dilute HCl acid solution

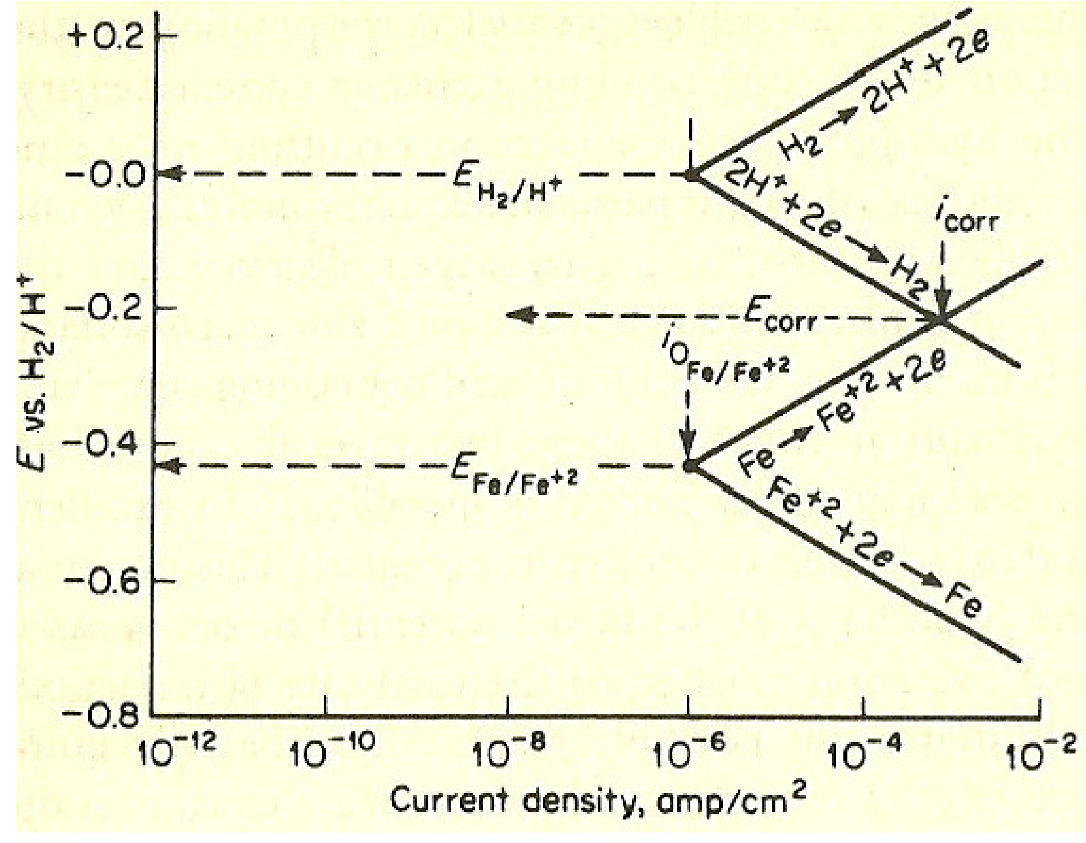


Fig.(14) Electrode kinetic behavior of pure iron in acid solution schematic.

Calculation of Corrosion rate from corrosion current (Faradays Law) :-

Faraday's Law states the 96,486.7 Coulombs of charge transfer will Oxidized or Reduce one gram Equivalent Weight of material involved in electrochemical reaction.

$$\frac{\text{(Avogadro's Number) } 6.023\times10^{23}\ \mathit{Atoms}\ /\ \text{Gram Atomic Weight}}{6.24\times10^{18}\ \mathit{Electrons}\ /\ \text{Coulomb}} \cong \frac{96{,}486.7\ \text{Coulombs}}{\mathit{Faraday}}$$

If we want to know how many Kilograms of iron (Fe) will be corroded by a direct current discharge from the metal's surface into the surrounding electrolyte at a current flow of one ampere for one year , using Faraday's law

$$\boxed{W = \frac{I\,t\,M}{n\,F} \quad \text{or} \quad W = \frac{i\,A\,t\,M}{n\,F}}$$

$$\frac{60\mathit{Seconds}}{\mathit{Minute}} \times \frac{60\mathit{Minutes}}{\mathit{Hour}} \times \frac{24\mathit{Hours}}{\mathit{Day}} \times \frac{365\mathit{Days}}{\mathit{Year}} \cong \frac{31{,}536{,}000\mathit{Secnds}}{\mathit{Year}}$$

$$1\,\mathit{Coulomb} = \text{Ampere - Second , Or 1 Ampere} = \text{1 Coulomb/Second}$$

$$\text{1 Ampere / year} = \frac{31{,}536{,}000\ \text{Seconds}}{\mathit{Year}} \times \frac{1\ \text{Coulomb}}{\mathit{Second}} \cong \frac{31{,}536{,}000\ \text{Coulomb}}{\mathit{Year}}$$

Since 1 coulomb will corrode (1gram equivalent weight of iron)

$$\frac{31{,}536{,}000\ \text{Coulombs/Year}}{96{,}486\ \text{Coulombs/Gram}} \cong \frac{326.9\ \text{gram equivalent weghts transferred}}{\mathit{Year}}$$

The gram equivalent weight of iron can be calculated as

$$\begin{aligned}\text{Gram Equivalent Weight (Fe)} &= \frac{\text{Gram Atomic Weight}}{\mathit{No}.\ \text{of Electrons Transferred / Fe Atom Corroded}}\\ &= \frac{55.85\ \text{Grams (Fe)}}{2\left(\text{Fe} \rightarrow \text{Fe}^{++} + 2\overline{e}\right)}\\ &= \frac{27.93\ \text{Grams}}{\text{Gram Equivalent Weight(Fe)}}\end{aligned}$$

The final calculation to obtain the Faradic consumption rate of iron is as follows :-

$$\frac{27.93\ \text{Grams (Fe)}}{\text{Gram Eq. Wt.}} \times \frac{326.9\ \text{Gram Eq. Wt. Transferred (Fe)}}{\text{Ampere - Year}} \cong \frac{9{,}130\ \text{Grams (Fe)}}{\text{Ampere - Year}}$$

Example problem

Rate of Oxidation Computation

Zinc experiences corrosion in an acid solution according to the reaction

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$$

The rates of both oxidation and reduction half-reactions are controlled by activation polarization.

(a) Compute the rate of oxidation of Zn (in mol/cm^2 –s) given the following activation polarization data:

For Zn	For Hydrogen
$E_{(Zn/Zn^{2+})} = -0.763\ \mathrm{V}$	$E_{(H^+/H_2)} = 0\ \mathrm{V}$
$i_o = 10^{-7}\ \mathrm{A/cm^2}$	$i_o =!0^{-10}\ \mathrm{A/cm^2}$
$\beta = +0.09$	$\beta = -0.08$

(b) Compute the value of the corrosion potential.

Solution:

(a) To compute the rate of oxidation for Zn, it is firist necessary to establish relationships in the form of Tafel equation for the potential of both oxidation and reduction reactions. Next, these two expressions are set equal to one another, and then we solve for the value of I that is the corrosion current density, i_C. Finally ,the corrosion rate may be calculated using Equation (1). The two potential expressions are follows: For hydrogen reduction.

$$E_H = E_{(H^+/H_2)} + \beta_H \log\left(\frac{i}{i_{oH}}\right)$$

And for Zn oxidation

$$E_{Zn} = E_{(Zn/Zn^{2+})} + \beta_{Zn} \log\left(\frac{i}{i_{oZn}}\right)$$

Now setting $E_H = E_{Zn}$ leads to

$$E_{(H^+/H_2)} + \beta_H \log\left(\frac{i}{i_{oH}}\right) = E_{(Zn/Zn^{2+})} + \beta_{Zn} \log\left(\frac{i}{i_{oZn}}\right)$$

And solving for log *i* (i.e., log i_C) leads to

$$\log i_C = \left(\frac{1}{\beta_{Zn} - \beta_H}\right)\left[E_{(H^+/H_2)} - E_{(Zn/Zn^{2+})} - \beta_H \log i_{oH} + \beta_{Zn} \log i_{oZn}\right]$$

$$= \left[\frac{1}{0.09 - (-0.08)}\right]\left[0 - (-0.763) - (-0.08)(\log 10^{-10}) + (0.09)(\log 10^{-7})\right]$$

$$= -3.924$$

Or

$$i_C = 10^{-3.924} = 1.19 \times 10^{-4}\ \text{A/cm}^2$$

And from eq.(1)

$$r_{red} = r_{oxid} = \frac{i_o}{nF}$$

$$= \frac{1.19 \times 10^{-4}\ \text{C/s-cm}^2}{(2)(96{,}500\ \text{C/mol})} = 6.17 \times 10^{-10}\ \text{mol/cm}^2\text{-s}$$

(b) Now it becomes necessary to compute the value of the corrosion potential E_C. This is possible by using either of the above equations for E_H or E_{Zn} and substituting for I the value determined above for i_C. Thus using the E_H expression yields

$$\begin{aligned} E_C &= E_{(H^+/H_2)} + \beta_H \log\left(\frac{i_C}{i_{oH}}\right) \\ &= 0 + (-0.08\ \mathrm{V}) \log\left(\frac{1.19\times10^{-4}\ \mathrm{A/cm^2}}{10^{-10}\ \mathrm{A/cm^2}}\right) \\ &= -0.486\ \mathrm{V} \end{aligned}$$

This is the same problem that is represented and solved graphically in the voltage-versus logarithm current density plot of Fig.(13). It is worth noting that the i_C and E_C we have obtained by this analytical treatment are in agreement with those values occurring at the intersection of the two line segments on the plot.