

## 2. Polarization and corrosion rates

### Polarization

When there is no net current flows from an electrode, then this electrode is at equilibrium state and its potential is the equilibrium potential ( $E^\circ$ ). When net current flows to or from its surface, the potential changes from  $E^\circ$  to  $E_i$ , the electrode is then said to be polarized and the process is termed as polarization. Polarization is measured in volts as follows:

$$\eta = E_i - E \quad (1)$$

Where:

$\eta$  = The overvoltage, and  $E_i$  = The polarization potential.

The accompanying Figure (1) shows polarization curves (E vs.  $\log(i)$ ) for the corrosion of metal in a reducing acid in which there are two exchange processes involving oxidation of  $M/M^+$  and reducing  $H^+/H_2$ . Polarization is divided into three main types:

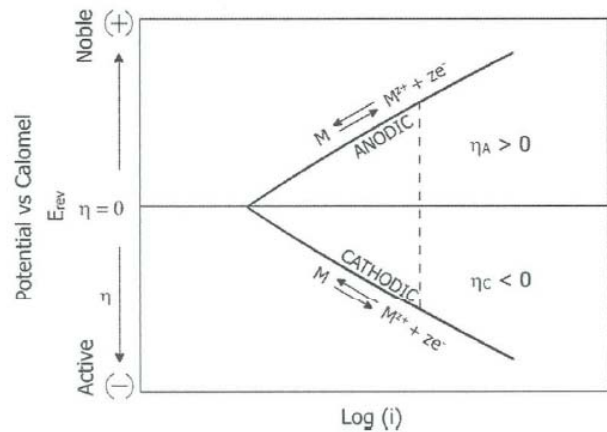
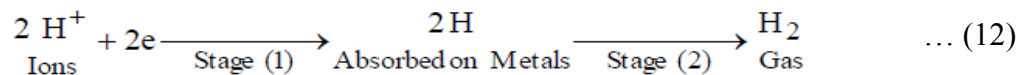


Figure 1 Polarization diagram (reversible electrode)

## 2. Polarization and corrosion rates

### 1. Activation Polarization ( $\eta_A$ )

This polarization is caused by a slow electrode reaction or stated in another way. The reaction at the electrode requires activation energy in order to go. The most important is that of hydrogen ion reduction at the cathode; reaction might be considered as:



Stage (1) occurs rapidly, whereas stage (2) is generally the slower and rate-controlling step. The activation overpotential, and hence the activation energy varies exponentially with the rate of charge transfer per unit area of electrode surface, as defined by the well-known Tafel equation:

$$\eta_a = \pm \beta \log \left( \frac{i}{i_o} \right) \quad \dots (13)$$

Where:

$i$  = The current density, and  
 $\beta$  = The Tafel constant being equal to  $\left( 2.303 \frac{RT}{\alpha Z F} \right)$

The Tafel constant ( $\beta$ ) varies with the nature of the electrode process and with the nature of the solution. Thus ( $\eta_A$ ) will be linearly related to ( $\log(i)$ ) at overpotential greater than 0.05 V and the position of the curve will be dependent on the equilibrium exchange current density ( $i_0$ ), the transfer coefficient ( $\alpha$ ) and the number of electrons ( $z$ ) involved in one act of the rate determining step.

The Tafel equation for a cathodic process can be expressed in the form:

$$\eta_{A,c} = \frac{R T}{\alpha z F} \ln i_0 - \frac{R T}{\alpha z F} \ln i_c \quad \dots (14)$$

Similarly for the anodic process:

$$\eta_{A,a} = -\frac{R T}{(1-\alpha) z F} \ln i_0 + \frac{R T}{(1-\alpha) z F} \ln i_a \quad \dots (15)$$

### Hydrogen Overpotential

The polarization term that controls the corrosion rate of many metals in deaerated water and in nonoxidizing acids is hydrogen overpotential. In accord with the previously discussed definition of polarization, hydrogen overpotential is the difference of potential between a cathode at which hydrogen is being evolved,  $E_i$ , and a hydrogen electrode at equilibrium in the same solution; that is,

$$\eta_{H_2} = E_i - E_{H_2}^{\circ} = E_i - (-0.059 \text{ pH}) = E_i + 0.059 \text{ pH}$$

## 2. Concentration Polarization ( $\eta_c$ ):

Concentration polarization is obtained when the rate of an electrode reaction is dependent on mass transfer, i.e. the rate at which the reactant is transported to the surface of the electrode and the rate at which the product is transported away from the electrode. For concentration polarization reaction current is given by

Fick's law:

$$|I| = z F D A \left( \frac{dC}{dx} \right) \quad \dots (16)$$

Or its equivalent

$$|I| = z F D A \left( \frac{C_b - C_s}{\delta} \right) \quad \dots (17)$$

The limiting current, i.e., the maximum current under diffusion control is obtained when  $C_s = 0$ .

$$|I_L| = z F D A \frac{C_b}{\delta} \quad \dots (18)$$

Or

$$|I_L| = z F A k C_b \quad \dots (19)$$

Where the mass transfer coefficient is defined as:

$$k = \frac{D}{\delta} \quad \dots (20)$$

The concentration polarization can also be expressed as:

$$\eta_c = \frac{R T}{z F} \ln \left( \frac{C_s}{C_b} \right) \quad \dots (21)$$

$$\text{Or } \boxed{\eta_c = \frac{R T}{z F} \ln \left( 1 - \frac{I}{I_L} \right)} \quad \dots (22)$$

Where:  $F$  = Faraday's constant (columbs/mole),  $D$  = Diffusivity ( $\text{cm}^2/\text{s}$ ),  $\delta$  = Diffusion layer thickness (cm),  
 $C_b$  = Bulk concentration ( $\text{gmole}/\text{cm}^3$ ),  $C_s$  = Surface concentration ( $\text{gmole}/\text{cm}^3$ ),  $A$  = Surface area ( $\text{cm}^2$ ). From  
equation (22) it can be seen that:

1. The term  $\left(1 - \frac{I}{I_L}\right)$  is equivalent to the term  $\left(\frac{C_s}{C_b}\right)$  in equation (21).
2. When  $I$  is very small in comparison with  $I_L$ , the concentration polarization is negligible.
3. When  $I$  approach  $I_L$  in magnitude, concentration polarization approaches infinity.

### 3. Resistance Polarization ( $\eta_R$ ):

The resistance polarization is the ohmic potential drop through a portion of the electrolyte surrounding the electrode, through a metal reaction product film on the surface or both. An ohmic potential drop always occurs between the working electrode and the capillary tip of reference electrode. The ohmic (i.e., solution) IR drop is given by:

$$IR_{\text{soln.}} = i\rho l = i/k \quad \dots (23)$$

Where:  $\rho$ =The specific resistance (i.e. resistivity) ( $\Omega\cdot\text{cm}$ ),  $k$ =The conductivity ( $\Omega^{-1}\cdot\text{cm}^{-1}$ ) or ( $\text{S}\cdot\text{cm}^{-1}$ );  
 $S$ =Siemens,  $l$ =The solution gap between the capillary tip and the working electrode (cm). Resistance polarization is important only at high current densities or in high resistance electrolyte solution. All of these three types of polarization will be present to a greater or less extent in most corrosion reactions.

$$\eta_{\text{total}} = \eta_A + \eta_c + \eta_R \quad \dots (24)$$

But if one is more influential than the others, then it will control the reaction rate.

## How Polarization Measured

Polarization can be measured using electrochemical corrosion cell and potentiostat as shown in figure 2.

Electrical connections are shown in figure 3.

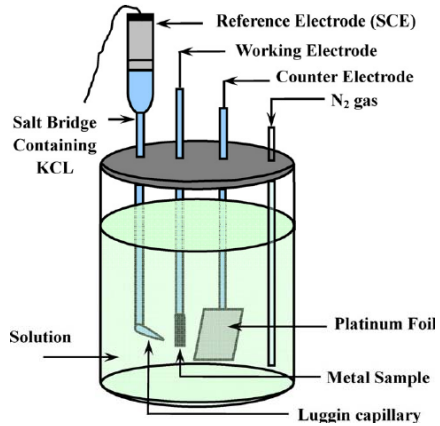


Figure 2 schematic diagram of polarization cell corrosion

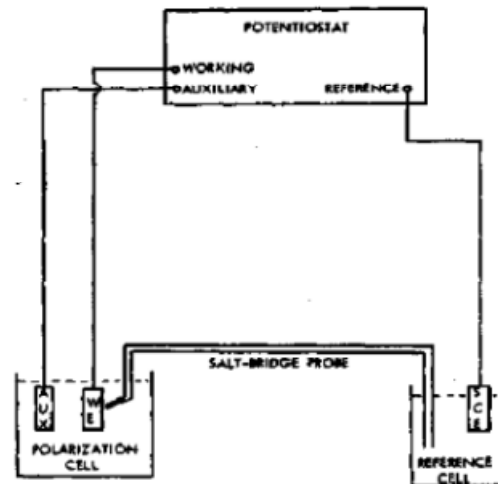


Figure 3 schematic potentiostatic anodic polarization wiring diagram

Polarization corrosion cell was equipped with several necks, which can be used according to the test conditions:

1. One for the working electrode (metal or test sample).
2. One for reference electrode (SCE, SHE, etc), for potential measurements.
3. One for thermometer, for temperature control.
4. Counter electrodes.

### 3. Corrosion Rate Measurements from Polarization Curve

Besides the weight loss technique there are other techniques used in corrosion rate measurements.

#### 1. LINEAR POLARIZATION TECHNIQUE

The linear polarization technique in principle is a convenient and rapid way for determining corrosion rates. The technique was started by *Wanger and Traud* who stated that the corrosion process with two coupled electrochemical reactions under activation control can be represented by:

$$i = i_{\text{Corr.}} \left[ \exp\left(\frac{\eta}{b_a}\right) - \exp\left(-\frac{\eta}{b_c}\right) \right] \quad \dots (25)$$

Equation 25 is derived and simplified by *Stern and Geary* for relatively small increment of the exponent (i.e., for potential within about 10 mV of the corrosion potential). The slope of this linear polarization is related to the kinetic parameters of the system as follows:

$$\frac{\Delta E}{\Delta i_{\text{app.}}} = \frac{b_a b_c}{2.303 I_{\text{corr.}} (b_a + b_c)} \quad \dots (26)$$

Where;

$b_a$  &  $b_c$  are the anodic and cathodic Tafel slopes respectively.

The *Stern and Geary* required both anodic and cathodic slopes. For accurate measurement, it is necessary to determine the values of  $b_a$  and  $b_c$ . For fast corrosion rate calculation assume the values of Tafel slopes in the range of 120 mV, then equation 26 reduced to:

$$\frac{\Delta E}{\Delta i_{app}} = \frac{0.026}{I_{corr.}} \Rightarrow I_{corr.} = \frac{0.026}{R_p} \quad \dots (27)$$

The ratio of the derivative of the overpotential to the current,  $\partial\eta/di$  when  $\eta \rightarrow 0$ , represents the resistance in Ohm's law and is often termed the charge-transfer resistance or the polarization resistance  $R_p$ .

$$R_p = d\eta/di \quad \text{for cathodic reaction from eq. 4} \quad \left[ \frac{di}{d\eta} \right] = -i^{\circ} \frac{anF}{RT}$$

### Example 7

The exchange current densities for a hydrogen-evolution reaction on three different metals are  $5 \times 10^{-4} \text{ A/cm}^2$ ,  $3 \times 10^{-7} \text{ A/cm}^2$ , and  $5 \times 10^{-11} \text{ A/cm}^2$ , respectively. Calculate the current densities and the polarization resistances if the reactions proceed at  $\eta = -0.08 \text{ V}$  versus SHE. The electrode surface area is  $1 \text{ cm}^2$  and  $\alpha = 0.5$ .

#### Solution:

The polarization resistance for a given area of the electrode is given by:

$$R_p = \frac{\left( \frac{d\eta}{di} \right)}{A}$$

The simplified form of the Butler-Volmer equation for the cathodic reaction can be written as:

$$\left[ \frac{di}{d\eta} \right] = -i^{\circ} \frac{anF}{RT}$$

The polarization resistance is calculated using the expression (A) and the given  $i^{\circ}$  values:

$$R_p = \frac{1}{A} \frac{1}{\left[ \frac{di}{d\eta} \right]} = -\frac{1}{AnFi^{\circ}} \quad (A)$$

$$R_{p_1} = 0.0513 \text{ k}\Omega$$

$$R_{p_2} = 0.0513 \text{ k}\Omega$$

$$R_{p_3} = 0.0513 \text{ k}\Omega$$

**Example 8**

Calculate the corrosion currents for the metals in **above** Example using the Stern-Geary equation for cathodic and anodic Tafel slopes of  $b_c = -0.1$  V and  $b_a = 0.1$  V. Estimate the corrosion rates in mpy.

**Solution:**

Corrosion currents:

$$I_{\text{corr}} = \frac{b_a \times b_c}{2.3(b_a + b_c)} \times \frac{1}{R_p}$$

$$I_{\text{corr}_1} = \frac{0.1\text{V} \times 0.1\text{V}}{2.3 \times (0.1\text{V} + 0.1\text{V})} \times \frac{1}{51.3\Omega} = 4.24 \times 10^2 \mu\text{A}/\text{cm}^2$$

$$I_{\text{corr}_2} = \frac{0.1\text{V} \times 0.1\text{V}}{2.3 \times (0.1\text{V} + 0.1\text{V})} \times \frac{1}{8.56 \times 10^4 \Omega} = 2.54 \times 10^{-1} \mu\text{A}/\text{cm}^2$$

$$I_{\text{corr}_3} = \frac{0.1\text{V} \times 0.1\text{V}}{2.3 \times (0.1\text{V} + 0.1\text{V})} \times \frac{1}{5.13 \times 10^8 \Omega} = 4.20 \times 10^{-5} \mu\text{A}/\text{cm}^2$$

Corrosion rates:

$$\text{C.R}_1 = \frac{0.131 \times (4.24 \times 10^2) \times (\text{E.W}_1)}{d_1}$$

$$\text{C.R}_2 = \frac{0.131 \times (2.54 \times 10^{-1}) \times (\text{E.W}_2)}{d_2}$$

$$\text{C.R}_3 = \frac{0.131 \times (4.20 \times 10^{-5}) \times (\text{E.W}_3)}{d_3}$$

**Example 9**

If the slope of the polarization curve is  $R_p = \Delta E / \Delta i = 2 \text{ mV} / \mu\text{A}/\text{cm}^2$  and the cathodic and anodic Tafel slopes are  $b_c = -0.1$  V and  $b_a = 0.1$  V, calculate the corrosion rate of Ni ( $d = 8.9 \text{ g}/\text{cm}^3$ ) in g/s.

**Solution:**

Using the Stern-Geary equation

$$I_{\text{corr}} = \frac{b_a \times b_c}{2.3(b_a + b_c)} \times \frac{\Delta i}{\Delta E} \quad I_{\text{corr}} = \frac{0.01\text{V}^2}{2.3 \times 0.2\text{V}} \times \frac{\mu\text{A}/\text{cm}^2}{2\text{mV}} \times \frac{1000\text{mV}}{1\text{V}} = I_{\text{corr}} = 10.87 \mu\text{A}/\text{cm}^2$$

$$\text{Because} \quad \frac{m}{t} = \frac{MI_{\text{corr}}}{nF} A$$

$$\text{CR} = \left[ \frac{58.6934 \text{ g/mol}}{2 \text{ eq/mol}} \right] \times [10.87 \mu\text{A}/\text{cm}^2] \times \frac{1 \text{ eq}}{96,500\text{C}} \times 1 \text{ cm}^2 \times \frac{1\text{C/s}}{10^6 \mu\text{A}} = 3.3 \times 10^{-9} \text{ g/s}$$



**Example 10**

The linear polarization slope for a tin electrode measured in tomato juice is  $5 \text{ mV}/(\mu\text{A}/\text{cm}^2)$ . Calculate the corrosion rate in  $(\text{g}/\text{m}^2 \text{ day})$ . Assume  $b_a = b_c = \pm 0.1 \text{ V}$ .

**Solution:**

$$R_p = \frac{\Delta E}{\Delta i} = 5 \frac{\text{mV}}{\mu\text{A}/\text{cm}^2} \quad I_{\text{corr}} = \frac{b_a \times b_c}{2.3(b_a + b_c)} \times \frac{\Delta i}{\Delta E} \quad I_{\text{corr}} = \frac{0.01 \text{ V}^2}{0.46 \text{ V}} \times \frac{\mu\text{A}/\text{cm}^2}{5 \text{ mV}} \times \frac{1000 \text{ mV}}{1 \text{ V}}$$

$$I_{\text{corr}} = 4.348 \mu\text{A}/\text{cm}^2$$

$$\text{CR} = [4.348 \mu\text{A}/\text{cm}^2] \left[ \frac{118.710 (\text{g}/\text{mol})}{2 (\text{eq}/\text{mol})} \right] \times \frac{1 \text{ cm}^2}{1 \times 10^{-4} \text{ m}^2} = 2.581 \times 10^6 \frac{\mu\text{Ag}}{\text{eq m}^2}$$

$$\text{CR} = 2.581 \times 10^6 \left( \frac{\mu\text{Ag}}{\text{eq m}^2} \right) \times \left( \frac{1 \text{ eq}}{96,487 \text{ C}} \right) \times \left( \frac{1 \text{ C}}{1 \times 10^6 \mu\text{A s}} \right) \times \left( \frac{3600 \text{ s}}{1 \text{ h}} \right) \times \left( \frac{24 \text{ h}}{1 \text{ day}} \right) = 2.31 \text{ g}/\text{m}^2 \text{ day}$$