CHAPTER 3

Electrochemical Kinetics of Corrosion

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Corrosion Engineering
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3.1 INTRODUCTION

This chapter outlines the basic aspects of interfacial electrochemical polarization and their relevance to corrosion. A discussion of the theoretical aspects of electrode kinetics lays a foundation for the understanding of the electrochemical nature of corrosion. Topics include mixed potential theory, reversible electrode potential, exchange current density, corrosion potential, corrosion current, and Tafel slopes. The theoretical treatment of electrochemistry in this chapter is focused on electrode kinetics, polarization behavior, mass transfer effects, and their relevance to corrosion. Analysis and solved corrosion problems are designed to understand the mechanisms of corrosion processes, learn how to control corrosion rates, and evaluate the protection strategies at the metal-solution interface [1–7].

3.2 OHMIC POLARIZATION

The passage of an electric current in any electrochemical corrosion system is associated with the change of the electrode potential from its initial equilibrium value. The potential of an electrolytic cell, \( E_{ec} \), at any current density is higher than the equilibrium cell potential, \( E_{cell} \).

\[
E_{ec} \geq E_{cell}
\]  
(3.1)

The difference between the electrolytic cell potential and the potential (voltage) when the current passes in the external circuit is due to ohmic losses. The main sources of ohmic losses are the resistance of the electrolyte, contact resistances of the leads, and the film formed on the electrode-electrolyte interface. The circuit ohmic resistance decreases the equilibrium potential by an amount equal to \( iR \), where “i” is the current passing between the working and counter electrode and \( R \) is the net resistance in the circuit. Current passes through the cell only when the voltage applied to the system consists of thermodynamically controlled equilibrium potential and the potential drop that compensates for the ohmic losses. The potential drop is not thermodynamically controlled and depends on the current density and the resistance in the circuit. It approaches zero when the current is shut off, and increases immediately when the current is switched on [8,9]. The \( iR \) drop in volts is equal to \( ioil/k \), where “\( io \)” is the current density in A/cm \(^2\), “\( i \)” is the thickness of the electrolyte in cm, and “\( k \)” is the specific conductivity of the electrolyte 1/\( \Omega \) cm. Various techniques are employed to measure the ohmic losses in an electrochemical cell. These measurement techniques include current interruption and four probe methods, among others that are discussed later in the book [8–10].

If the electrochemical system generates a current (galvanic cell), then the experimentally observed cell potential decreases with the passage of current. In this case, the resistance in the galvanic cell controls the voltage drop, which compensates for the resistance inside the cell and introducing a loss in electrical energy production. When a net current
flows through any corrosion system, the main factor causing a change in the cell voltage is not the voltage drop, but rather the variation of the potential with respect to the applied current density, which is also called the electrode polarization.

### 3.3 Electrochemical Polarization

When a metal, M, is immersed in a solution containing its ions, M⁺, several reactions may occur. The metal atoms may lose electrons (oxidation reaction) to become metallic ions, or the metal ions in solution may gain electrons (reduction reaction) to become solid metal atoms. The equilibrium conditions across the metal–solution interface controls which reaction, if any, will take place. When the metal is immersed in the electrolyte, electrons will be transferred across the interface until the electrochemical potentials or chemical potentials (Gibbs free–energies) on both sides of the interface are balanced, that is, \( \mu_{\text{solution}} = \mu_{\text{electrode}} \) until thermodynamic equilibrium is reached. The charge transfer rate at the electrode-electrolyte interface depends on the electric field across the interface and on the chemical potential gradient. At equilibrium, the net current is zero and the rates of the oxidation and reduction reactions become equal. The potential when the electrode is at equilibrium is known as the reversible half-cell potential or equilibrium potential, \( E_{\text{eq}} \). The net equivalent current that flows across the interface per unit surface area when there is no external current source is known as the exchange current density, \( i^o \).

The difference between the potential, \( E \), when a net current flows through the electrochemical cell and the reversible half-cell potential, \( E_{\text{eq}} \), is called the electrode polarization or simply the overpotential or overvoltage, \( \eta \). The overvoltage represents the extent to which the electrode solution interface departs from the equilibrium potential value.

\[
\eta = E - E_{\text{eq}} \tag{3.2}
\]

The overvoltage depends on the current density. When there is no net current flow, the overvoltage is equal to zero. Electrochemical processes are heterogeneous reactions consisting of consecutive steps. The overvoltage controls the kinetics of the charge-transfer reaction at the interface and is associated with the slowest step, abbreviated as the rate determining step.

Electrochemical polarization experiments are performed to study the kinetics of charge-transfer reactions at the electrode-electrolyte interface. When cathodic current is applied to the electrode, the electrons accumulate in the metal as a result of the slow charge transfer. This phenomenon causes the cathodic polarization, \( \eta_c \), to be always negative. Conversely, when electrons are removed from the metal as in the case of anode polarization, the polarization is always positive.

The transport of reactants to and from the electrode-electrolyte interface occurs during any electrochemical process. The electrode reactions involve at least one charge
transfer across the electrode-electrolyte interface. Due to the passage of current, these steps control the concentration of the reactants near the electrode. The change in composition alters the electrode potential resulting in electrode polarization. The concentration overvoltage, $\eta_{\text{conc}}$, results from a slow transport of reactants to and from the electrode interface and from the chemical transformation preceding the transport of ions. A special case of concentration polarization occurs when mass transport is an irreversible process, corresponding to the transport overpotential or diffusion overpotential, $\eta_d$. When a slow chemical reaction causes concentration polarization and all other processes proceed reversibly, it is called chemical or reaction overvoltage, $\eta_r$. When all the steps of the electrode reaction except the charge transfer proceed reversibly, the electrode polarization is called the charge transfer or electrochemical overpotential, $\eta_e$. If the rate-determining step is the incorporation of metallic ions in the electrode crystal lattice, the electrode polarization is called the phase overpotential, $\eta_{\text{ph}}$. The departure of the operating electrode potential from the equilibrium potential value results from superposition of all types of overpotentials,

$$\eta = \eta_d + \eta_r + \eta_e + \eta_{\text{ph}}$$  (3.3)

The electrochemical ($\eta_e$) and the phase overpotentials ($\eta_{\text{ph}}$) are called the activation polarization, $\eta_{\text{ac}}$. The overall overvoltage is the sum of the concentration polarization and the activation polarization:

$$\eta = \eta_{\text{conc}} + \eta_{\text{ac}}$$  (3.4)

where $\eta_{\text{conc}}$ is the sum of the diffusion and the reaction overpotential.

The rate of any electrochemical reaction, and consequently the current, is controlled, in part, by the rate of the charge-transfer reaction and the rate of transport of the electroactive species to the electrode surface. In this chapter, we will assume that the solution is homogeneous, so that the surface concentration of the ions is equal to the concentration in the bulk solution. This would approximately be the case when the solution is stirred and the transport of the ions to the electrode is fast. Under these conditions, the current is controlled only by the rate of the electron transfer at the electrode. If the electron transfer reaction is described by Eq. (3.5), the rate of the cathodic reaction is first order in concentration of oxidized species at the electrode-electrolyte interface.

$$\text{O} + e^{-} \xrightarrow{k_c} \text{R}$$  (3.5)

$\text{O}$ and $\text{R}$ are oxidized and reduced species, respectively. The cathodic rate is defined by $k_c C_\text{O}$, where $k_c$ is the cathodic reaction rate constant and $C_\text{O}$ is the concentration of oxidized species. The rate of oxidation at the anode is first order in the concentration of reduced species at the electrode-electrolyte interface, $\text{R}$, and is given by $k_a C_\text{R}$, where $k_a$ is the anodic reaction rate constant and $C_\text{R}$ is the concentration of reduced species.
The heterogeneous rate constants, \( k_a \) and \( k_c \), have units of m/s. The net flux of "O" at the electrode surface (conversion rate of O to R) is the difference between the cathodic and the anodic rates, which is proportional to the net current, \( i \), that passes in the circuit. Thus,

\[
\text{Net conversion rate} = k_c C_O - k_a C_R
\]  

(3.6)

or

\[
i = FA[k_c C_O - k_a C_R] 
\]

(3.7)

\( F \) in Eq. (3.7) is Faraday’s constant, while \( A \) is the electrode surface area. At equilibrium, the net current flow is equal to zero; that is, the current flow for the forward reaction (product formation) is equal to the current flow for the reverse reaction (reactant formation from the products) in an electrochemical reaction involving oxidation and reduction reactions. At equilibrium, the current flow is not zero for the forward and reverse reactions. The passage of current in either forward or reverse reaction is equal to the exchange current density of the overall redox reaction.

In most cases, the reaction rate constants “\( k \)” follows the Arrhenius equation:

\[
k = Z \exp \left( \frac{-\Delta G^*}{RT} \right)
\]

(3.8)

where \( Z \) is the preexponential factor, \( \Delta G^* \) is the activation energy, \( R \) is the universal gas constant, and \( T \) is the absolute temperature. If this is the case, and the activation energy is independent of temperature, then a plot of \( \ln k \) vs. \( 1/T \) would be a straight line with a slope \( -\Delta G^*/R \).

The exponential term in Eq. (3.8) is related to the probability of surmounting the energy barrier defined by the standard free energy of activation \( \Delta G_o^* \). The preexponential factor, \( Z \), is known as the frequency factor, which indicates the number of attempts needed to surmount the standard free energy of activation. In this chapter, \( Z \) is treated as an empirical parameter with units of m/s.

From transition state theory, the temperature dependence of anodic and cathodic rate constants is given by:

\[
k_c = Z \exp \left( \frac{-\Delta G_c^*}{RT} \right)
\]

(3.9a)

\[
k_a = Z \exp \left( \frac{-\Delta G_a^*}{RT} \right)
\]

(3.9b)

Under equilibrium conditions, the ratio of the concentration of the oxidized and reduced species is given by the Nernst equation:

\[
e_{eq} = e^o + \frac{RT}{F} \ln \frac{C_O}{C_R}
\]

(3.10)
where $e_{eq}$ and $e^o$ are the equilibrium and standard half-cell potentials, respectively. Taking the logarithm of Eqs. (3.9a) and (3.9b) and substituting into Eq. (3.8), one obtains:

$$\frac{\Delta G_c^* - \Delta G_a^*}{RT} = \frac{C_O}{C_R} = \left(\frac{k_a^o}{k_c^o}\right) \exp\left(\frac{nF}{RT}\right)(e_{eq} - e^o)$$

(3.11)

In Eq. (3.11) $n$ is the number of electrons, while $k_a^o$ and $k_c^o$ are rate constant at zero current.

Combining Eq. (3.11) with the Nernst equation, one obtains:

$$\Delta G_c^* - \Delta G_a^* = nF(e_{eq} - e^o)$$

(3.12)

The electrochemical free energy change at equilibrium and reduction is depicted in Fig. 3.1. As shown in Fig. 3.1a, the difference between the cathodic and anodic activation

![Fig. 3.1](image_url)

Fig. 3.1 Electrochemical free energy change (a) at equilibrium and (b) when the oxidized species are reduced.
free energies for the redox reaction in Eq. (3.5) is equal to the standard free energy. Curve “R” represents the potential energy curve of reduced species at the equilibrium potential of the redox couple, while curve “O” stands for the potential energy curve for the species in their oxidized form.

The rates of the cathodic and anodic reaction, shown in Eq. (3.12), depend on the electrode potential. If the electrode potential shifts in the cathodic direction, favoring the cathodic reaction in Eq. (3.5), the free energy of the redox system changes by an amount of $-nF\Delta E$, lowering the potential energy curve of the reduced species to a new position represented by curve P in Fig. 3.1b.

For the cathodic and anodic activation energies, one can assume simple linear relationships:

\[
\Delta G^c = \Delta G^o_c + \alpha_c nF(e_{eq} - e^o) \quad (3.13)
\]
\[
\Delta G^a = \Delta G^o_a - \alpha_a nF(e_{eq} - e^o) \quad (3.14)
\]

In Eq. (3.13), $\alpha_c$ is the fraction of the total free energy ($-nF\Delta E$) that decreases the energy barrier for the cathodic reaction, while $\alpha_a = 1 - \alpha_c$ is the fraction that increases the anodic potential barrier in Fig. 3.1b. The parameters $\alpha_c$ and $\alpha_a$ are called the cathodic and anodic transfer coefficients. As shown in Fig. 3.1b, they are a measure of energy barrier symmetry of the cathodic and anodic potential energy curves. If under equilibrium conditions, the cathodic and anodic activation free energies are substituted into Eqs. (3.9a) and (3.9b), one obtains:

\[
k^o_c = k_0 \exp\left(-\frac{\alpha_c nF(e_{eq} - e^o)}{RT}\right) \quad (3.15)
\]
\[
k^o_a = k_0 \exp\left(-\frac{\alpha_a nF(e_{eq} - e^o)}{RT}\right) \quad (3.16)
\]

where

\[
k_0 = Z \exp\left(-\frac{\Delta G^o}{RT}\right) \quad (3.17)
\]

Current flows through the corrosion system (electrochemical cell) only when the redox reaction is not at equilibrium. The difference between the operating electrode potential, $E$, and the equilibrium potential, $e_{eq}$, is defined as the electrode polarization, $\Delta E$. Thus, the electrode polarization is a deviation from the equilibrium potential in the presence of current. When a cathodic current is imposed, the potential is displaced to the negative side, causing cathodic polarization to be negative. When an anodic current is applied, polarization is positive. The electrode polarization and defined nature of the limiting step is called electrode overpotential or overvoltage.

\[
\eta = E - e_{eq} \quad (3.18)
\]
The rate constants at nonequilibrium conditions are defined as:

\[ k_c = k^0_c \exp \left( -\frac{\alpha_c nF\eta}{RT} \right) \] (3.19)
\[ k_a = k^0_a \exp \left( \frac{\alpha_a nF\eta}{RT} \right) \] (3.20)

Thus the rate of the anodic and cathodic reactions can be expressed as:

\[ i_a = Fk^0_a C_R \exp \left( \frac{-\alpha_c F(E - e_{eq})}{RT} \right) \] (3.21a)
\[ i_c = Fk^0_c C_O \exp \left( \frac{-\alpha_c F(E - e_{eq})}{RT} \right) \] (3.21b)

Substituting the rate constant at nonequilibrium conditions into Eq. (3.7): 

\[ i = FA \left[ k^0_c C_O \exp \left( -\frac{\alpha_c F\eta}{RT} \right) - k^0_a C_R \exp \frac{\alpha_a F\eta}{RT} \right] \] (3.22)

or

\[ i = i^0 \left[ \frac{C_O}{C_O^b} \exp \left( -\frac{\alpha_c F\eta}{RT} \right) - \frac{C_R}{C_R^b} \exp \frac{\alpha_a F\eta}{RT} \right] \] (3.23)

where \( i^0 \) is the exchange current density, while \( C_O^b \) and \( C_R^b \) are the concentrations of the oxidized and reduced species in the bulk of the solution at equilibrium. At equilibrium conditions:

\[ i_c = i_a = i^0 \] (3.24)
\[ i = i^0 - i = 0 \] (3.25)

\[ i^0 = i_{c, eq} = FAK_0 C_O^b \exp \left( -\frac{\alpha_c F(e_{eq} - e^o)}{RT} \right) \] (3.26)
\[ i^0 = -i_{a, eq} = FAK_0 C_R^b \exp \left( \frac{\alpha_a F(e_{eq} - e^o)}{RT} \right) \] (3.27)

In the case of energy producing power sources, the equilibrium shifts to one side, resulting in the flow of net current and the subsequent loss of equilibrium at the electrode. A system of this nature is said to be polarized. The net current that flows through the polarized system at any given overpotential is \( i = (i_a - i_c) \). Assuming fast transport, the concentrations of the electroactive species in the bulk and at the electrode interface are equal which reduces Eq. (3.23) to the Butler-Volmer equation (3.28), which is a fundamental equation in electrode kinetics.
The exchange current density, $i^o$, represents the oxidation and the reaction rates at equilibrium. Exchange current densities for hydrogen and oxygen evolution reaction on different metals are given in Table 3.1 [1]. The magnitude of the exchange current density varies in Table 3.1 depending on the metal electrode. The experimentally measured exchange current density for hydrogen evolution on Ni in 1 M HCl is $2 \times 10^{-11} \text{ A/cm}^2$, while Pt is eight orders of magnitude higher at $10^{-3} \text{ A/cm}^2$. The exchange current density is a function of the ratio of the oxidized and reduced species and the temperature. Because it is expressed in terms of geometric surface area, the exchange current density also depends on the surface roughness.

3.3.1 Special cases of Butler-Volmer equation-high field approximation

The electrode overpotentials, $\eta$, and its effect on current, $i$, are very significant in electrochemistry and corrosion engineering. When $\eta$ is large, one of the exponential terms of the Butler–Volmer equation will be negligible as compared to the other. For example, when the overpotential is large and cathodic (negative), the anodic term in Eq. (3.28) is negligible, and we can approximate Eq. (3.28) using the form:

$$i_c = i^o \exp\left(\frac{-\alpha_c F \eta}{RT}\right)$$

or

$$\eta = \alpha_c nF \ln \frac{i_c}{i^o}$$

Equation (3.30) is the Tafel equation, named for the German scientist who discovered the relationship between the current equivalent to the rate of a single reaction on a metal surface and the potential of the metal. By defining the Tafel constants

$$a_c = 2.3 \frac{RT}{\alpha_c nF} \log i^o$$

and

$$b_c = -2.3 \frac{RT}{\alpha_c nF}$$

Equation (3.30) can be simplified to:

$$\eta = a_c + b_c \log i$$

Plots of $\eta$ vs. log $i$ (called Tafel plots) at high overpotentials would be straight lines, from which the constants $a_c$ and $b_c$ could be evaluated. Tafel plots have been long known to fit
<table>
<thead>
<tr>
<th>Electrode</th>
<th>Solution</th>
<th>( i_o (A/cm^2) )</th>
<th>( b_c ) (V)</th>
<th>( b_a ) (V)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
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<td>Pt</td>
<td>1 N HCl</td>
<td>10^{-2}</td>
<td>0.03</td>
<td></td>
<td>[11]</td>
</tr>
<tr>
<td></td>
<td>0.1 N NaOH</td>
<td>0.7 \times 10^{-3}</td>
<td>0.11</td>
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<td>[11]</td>
</tr>
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<td>Pd</td>
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<td>[11]</td>
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<tr>
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<td>0.05</td>
<td></td>
<td>[11]</td>
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<tr>
<td>Ta</td>
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<td>10^{-4}</td>
<td>0.08</td>
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<td>[11]</td>
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<tr>
<td>W</td>
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<td>10^{-4}</td>
<td>0.11</td>
<td></td>
<td>[11]</td>
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<tr>
<td>Ag</td>
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<td>0.12 N H_2SO_4</td>
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<td>0.10</td>
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<td>[11]</td>
</tr>
<tr>
<td>Bi</td>
<td>1 N HCl</td>
<td>10^{-6}</td>
<td>0.10</td>
<td></td>
<td>[11]</td>
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<td>Nb</td>
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<td>[11]</td>
</tr>
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<td>0.15</td>
<td></td>
<td>[11]</td>
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<td></td>
<td>0.52 N H_2SO_4</td>
<td>2 \times 10^{-5}</td>
<td>0.11</td>
<td></td>
<td>[12]</td>
</tr>
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<td></td>
<td>4% NaCl, pH 1-4</td>
<td>10^{-6}</td>
<td>0.10</td>
<td></td>
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<tr>
<td>Cu</td>
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<td>2 \times 10^{-6}</td>
<td>0.12</td>
<td></td>
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</tr>
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<td></td>
<td>[11]</td>
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<td></td>
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</tr>
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<td>Be</td>
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<td>0.12</td>
<td></td>
<td>[11]</td>
</tr>
<tr>
<td>Sn</td>
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<td>0.15</td>
<td></td>
<td>[11]</td>
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<td>0.20</td>
<td></td>
<td>[11]</td>
</tr>
<tr>
<td>Zn</td>
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<td>2 \times 10^{-10}</td>
<td>0.12</td>
<td></td>
<td>[11]</td>
</tr>
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<td>Hg</td>
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<td>0.12</td>
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<td>[11]</td>
</tr>
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<td>2 \times 10^{-12}</td>
<td>0.12</td>
<td></td>
<td>[11]</td>
</tr>
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<td></td>
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<td>3 \times 10^{-14}</td>
<td>0.10</td>
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<td>[11]</td>
</tr>
<tr>
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<td>0.12</td>
<td></td>
<td>[11]</td>
</tr>
<tr>
<td>Reaction:</td>
<td>( O_2 + 4H^+ + 4e^{-} \rightarrow 2H_2O )</td>
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<td></td>
<td></td>
<td></td>
</tr>
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<td>Pt</td>
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<td>9 \times 10^{-11}</td>
<td>0.10</td>
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</tr>
<tr>
<td>Reaction:</td>
<td>( O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^- )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>0.1 N NaOH</td>
<td>4 \times 10^{-12}</td>
<td>0.05</td>
<td></td>
<td>[11]</td>
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<tr>
<td>Au</td>
<td>0.1 N NaOH</td>
<td>5 \times 10^{-12}</td>
<td>0.05</td>
<td></td>
<td>[11]</td>
</tr>
<tr>
<td>Reaction:</td>
<td>( Cl_2 + 2e^- \rightarrow 2Cl^- )</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>1 N HCl</td>
<td>5 \times 10^{-3}</td>
<td>0.11</td>
<td>0.130</td>
<td>[11]</td>
</tr>
<tr>
<td>Reaction:</td>
<td>( M \rightarrow Mn^{+} + ne^- )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>0.52 N H_2SO_4</td>
<td>10^{-7}</td>
<td>0.060</td>
<td>[12]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.52 N H_2SO_4</td>
<td>10^{-10}</td>
<td>0.039</td>
<td>[12]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.63 N Fe_2SO_4</td>
<td>3 \times 10^{-9}</td>
<td>0.060-</td>
<td>[14]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4% NaCl, pH 1-4</td>
<td></td>
<td>0.075</td>
<td></td>
<td>[15]</td>
</tr>
<tr>
<td></td>
<td>0.3 N H_2SO_4</td>
<td></td>
<td>0.068</td>
<td></td>
<td>[16]</td>
</tr>
<tr>
<td></td>
<td>0.5 M FeSO_5, 0.1 M NaHSO_4</td>
<td>3 \times 10^{-10}</td>
<td>0.030</td>
<td>[17]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Perchlorate</td>
<td></td>
<td>0.030</td>
<td>[18]</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.001 N Cu(NO_3_2)</td>
<td>10^{-9}</td>
<td></td>
<td></td>
<td>[11]</td>
</tr>
</tbody>
</table>

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experimental data obtained in studies of activation overpotential (such as the evolution of hydrogen and oxygen at various electrodes). Equation (3.32) may also be written in the form

$$\eta = b_c \log \left( \frac{i}{i_0} \right)$$  \hspace{1cm} (3.33)

The overpotential, \(\eta\), is occasionally called the activation overpotential and ignores the contribution of the overpotential changes due to concentration gradients. The use of activation overpotential normally occurs when the concentration of ions in solution is very high or when there is enough forced convection to minimize concentration gradients. These conditions are approached in experimental setups like rotating disk electrodes.

Similar expressions are obtained when the overpotential is large and anodic (positive), resulting in the cathodic term being eliminated. When the anodic process takes place,

$$i = -i_a = \overleftrightarrow{i}$$  \hspace{1cm} (3.34)

then,

$$i_a = i^o \exp \left( \frac{(1-\alpha)nF\eta}{RT} \right)$$  \hspace{1cm} (3.35)

and

$$\eta = \frac{2.3RT}{(1-\alpha)nF} \log i^o + \frac{2.3RT}{(1-\alpha)nF} \log i_a$$  \hspace{1cm} (3.36)

The Tafel relationship for the anodic process becomes:

$$\eta = a_a + b_a \log i$$  \hspace{1cm} (3.37)

where

$$a_a = -2.3 \frac{RT}{(1-\alpha)nF} \log i^o$$  \hspace{1cm} (3.38a)

and

$$b_a = 2.3 \frac{RT}{(1-\alpha)nF}$$  \hspace{1cm} (3.38b)

Comparison of the anodic and cathodic Tafel constants shows that when \(\alpha = 0.5\), \(a_c = -a_a\); \(b_c = -b_a\). Tables 3.2 and 3.3 list values of the Tafel constants for cathodic hydrogen evolution at \(T = 20 \pm 2 \, ^\circ\text{C}\) on different metals and the effect of electrode materials and solution composition on oxygen overpotential [21]. The Tafel equation has been confirmed for numerous cathodic and anodic reactions, and its use is illustrated in the examples and case studies that follow.
### Table 3.2 Values of Tafel Constants for Cathodic Hydrogen Evolution on Different Metals, $T = 20 \pm 2 ^\circ C$ [21]

<table>
<thead>
<tr>
<th>Metal</th>
<th>Acidic Solutions</th>
<th>Alkaline Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a$</td>
<td>$b$</td>
</tr>
<tr>
<td>Ag</td>
<td>0.95</td>
<td>0.100</td>
</tr>
<tr>
<td>Al</td>
<td>1.00</td>
<td>0.100</td>
</tr>
<tr>
<td>Au</td>
<td>0.40</td>
<td>0.120</td>
</tr>
<tr>
<td>Be</td>
<td>1.08</td>
<td>0.120</td>
</tr>
<tr>
<td>Bi</td>
<td>0.84</td>
<td>0.120</td>
</tr>
<tr>
<td>Cd</td>
<td>1.40</td>
<td>0.120</td>
</tr>
<tr>
<td>Co</td>
<td>0.62</td>
<td>0.140</td>
</tr>
<tr>
<td>Cu</td>
<td>0.87</td>
<td>0.120</td>
</tr>
<tr>
<td>Fe</td>
<td>0.70</td>
<td>0.120</td>
</tr>
<tr>
<td>Ge</td>
<td>0.97</td>
<td>0.120</td>
</tr>
<tr>
<td>Hg</td>
<td>1.41</td>
<td>0.114</td>
</tr>
<tr>
<td>Mn</td>
<td>0.8</td>
<td>0.100</td>
</tr>
<tr>
<td>Mo</td>
<td>0.66</td>
<td>0.080</td>
</tr>
<tr>
<td>Nb</td>
<td>0.8</td>
<td>0.100</td>
</tr>
<tr>
<td>Ni</td>
<td>0.63</td>
<td>0.110</td>
</tr>
<tr>
<td>Pb</td>
<td>1.56</td>
<td>0.110</td>
</tr>
<tr>
<td>Pd</td>
<td>0.24</td>
<td>0.030</td>
</tr>
<tr>
<td>Pt</td>
<td>0.10</td>
<td>0.030</td>
</tr>
<tr>
<td>Sb</td>
<td>1.00</td>
<td>0.110</td>
</tr>
<tr>
<td>Sn</td>
<td>1.20</td>
<td>0.130</td>
</tr>
<tr>
<td>Ti</td>
<td>0.82</td>
<td>0.140</td>
</tr>
<tr>
<td>Tl</td>
<td>1.55</td>
<td>0.140</td>
</tr>
<tr>
<td>W</td>
<td>0.43</td>
<td>0.100</td>
</tr>
<tr>
<td>Zn</td>
<td>1.24</td>
<td>0.120</td>
</tr>
</tbody>
</table>

### Table 3.3 The Effect of Electrode Material and Solution Composition on Oxygen Overpotential [21]

<table>
<thead>
<tr>
<th>Metal</th>
<th>Solution</th>
<th>$T$ (°C)</th>
<th>$b/2.303$</th>
<th>$a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>0.005-0.05 N H$_2$SO$_4$</td>
<td>25</td>
<td>10$^{-7}$-10$^{-4}$</td>
<td>(3/2 RT)/F</td>
</tr>
<tr>
<td>Pt</td>
<td>0.1 N H$_2$SO$_4$</td>
<td>35</td>
<td>10$^{-7}$-10$^{-2}$</td>
<td>2RT/F</td>
</tr>
<tr>
<td>Pt</td>
<td>0.1 N NaOH</td>
<td>25</td>
<td>-</td>
<td>RT/F</td>
</tr>
<tr>
<td>Au</td>
<td>0.1-1.0 N H$_2$SO$_4$</td>
<td>25</td>
<td>3 × 10$^{-2}$-10$^{-2}$</td>
<td>(3/4 RT)/F</td>
</tr>
<tr>
<td>Au</td>
<td>0.1 N NaOH</td>
<td>25</td>
<td>-</td>
<td>RT/F</td>
</tr>
<tr>
<td>Pb</td>
<td>3.8 N H$_2$SO$_4$</td>
<td>30</td>
<td>-</td>
<td>2RT/F</td>
</tr>
<tr>
<td>Pt, PbO$_2$ ($\alpha$)</td>
<td>4.4 N H$_2$SO$_4$</td>
<td>31.8</td>
<td>10$^{-4}$-2 × 10$^{-3}$</td>
<td>(3/4 RT)/F</td>
</tr>
<tr>
<td>Pt, PbO$_2$ ($\beta$)</td>
<td>4.4 N H$_2$SO$_4$</td>
<td>31.8</td>
<td>7 × 10$^{-5}$-2 × 10$^{-3}$</td>
<td>2RT/F</td>
</tr>
<tr>
<td>Ni</td>
<td>7.5 N KOH</td>
<td>25</td>
<td>5 × 10$^{-6}$-10$^{-3}$</td>
<td>(1/2 RT)/F</td>
</tr>
<tr>
<td>Ni</td>
<td>7.5 N KOH</td>
<td>25</td>
<td>10$^{-3}$-5 × 10$^{-2}$</td>
<td>3RT/F</td>
</tr>
<tr>
<td>Ni</td>
<td>7.5 N KOH</td>
<td>25</td>
<td>5 × 10$^{-2}$-3 × 10$^{-1}$</td>
<td>RT/F</td>
</tr>
<tr>
<td>Fe</td>
<td>pH = 2</td>
<td>5</td>
<td>3 × 10$^{-6}$-10$^{-4}$</td>
<td>(1/2 RT)/F</td>
</tr>
</tbody>
</table>
Example 3.1
The potential of an iron electrode when polarized as a cathode in an aqueous medium is $-0.716 \text{ V vs. SCE}$. What would be the value of the hydrogen overpotential of this electrode in an electrolyte with a pH of 2.0?

Solution:
The hydrogen overpotential, $\eta$, is the difference between the potential of iron electrode ($E = -0.716 \text{ V vs. SCE}$) and the potential of the hydrogen reaction.

$$\eta = E - e_{eq}$$

For the hydrogen reaction $2H^+ + 2e^- \rightarrow H_2$, $e_{H^+|H_2}^0 = 0.00 \text{ V vs. SHE}$ or $e_{H^+|H_2}^0 = -0.241 \text{ V vs. SCE}$

$$e_{eq,H^+|H_2} = e_{H^+|H_2}^0 - 0.059(\text{pH}) = -0.241 - (0.059 \times 2)$$
$$= -0.359 \text{ V vs. SCE}$$

The hydrogen overpotential is the difference of the potential of iron electrode ($-0.716 \text{ V vs. SCE}$) and the potential of the hydrogen reaction.

$$\eta = -0.716 - (-0.359) = -0.357 \text{ V}$$

Example 3.2
The potential of an iron electrode when cathodically polarized in an aqueous medium is $-0.75 \text{ V vs. SHE}$. Determine the hydrogen overpotential in electrolytes with pH between 1 and 6.

Solution:

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

$$e_{eq,H^+|H_2} = e_{H^+|H_2}^0 - 2.303 \frac{RT}{nF} \log \left( \frac{a_{H_2}}{(a_{H^+})^2} \right)$$

The hydrogen overpotential is the difference of the potential of the iron electrode and the potential of hydrogen reaction.

$$\eta = E - e_{eq}$$

$$\eta_{eq,H^+|H_2} = 0 - 0.059(\text{pH})$$

$$e_{eq,H^+|H_2} = -0.059(\text{pH})$$

$$\eta_{H_2} = -0.75 - e_{eq,H^+|H_2}$$

$$\eta_{H_2} = -0.75 - (-0.059(\text{pH}))$$

At a pH of 1,

$$\eta_{H_2} = -0.75 + 0.059(1) = -0.691 \text{ V}$$

The effect of pH on the hydrogen overpotential of the iron electrode in an aqueous medium is shown in Fig. 3.2.
Example 3.3

Oxygen evolves at a platinum anode at pH 8 when a potential of 0.515 V with respect to the saturated calomel electrode is applied. The reaction occurs at unit pressure of oxygen. The potential of the standard calomel electrode is 0.241 V vs. SHE.

(a) Calculate the overpotential of the oxygen evolution reaction and predict whether or not the reaction will take place at this potential.

(b) Calculate the overpotential of the reaction at pH 6, 7, 9, and 10 and determine whether the oxygen reduction reaction will occur if the applied potential of the platinum remains at 0.515 V vs. SCE. Given: The standard electrode potential for oxygen evolution reaction at pH 14 is 0.401 V vs. SHE.

Solution:

(a) The standard electrode potential for oxygen evolution reaction at pH 14 is 0.401 vs. SHE. At pH = 8,

\[
\varepsilon_{\text{eq,}O_2|\text{OH}^-} = \varepsilon_{O_2|\text{OH}^-} - \frac{0.059}{n} \log(a_{\text{OH}^-}) = 0.401 + 0.059(14 - \text{pH}) = 0.401 + 0.059(14 - 8)
\]

\[
\varepsilon_{\text{eq,}O_2|\text{OH}^-} = 0.755 \text{ V vs. SHE}
\]

The oxygen equilibrium potential at a pH of 8 is estimated to be 0.755 vs. SHE. Because the potential of Pt electrode is 0.515 V vs. SCE when normalized to the SHE scale, it becomes 0.756 vs. SHE. The oxygen overpotential is only 0.001 V and the oxygen evolution reaction will occur at pH slightly above 8.

(b) A plot of pH vs. oxygen overpotential is constructed using the following expression:

\[\eta = E - \varepsilon_{\text{eq,}O_2|\text{OH}^-}\]
For example, at pH $\approx 6$, the overpotential, $\eta$, is,

$$\eta = \frac{-0.756 - e_{\text{eq}, \text{O}_2 | \text{OH}^-}}{C_0^{e_{\text{eq}, \text{O}_2 | \text{OH}^-}}}$$

$$\eta = -0.756 - [0.401 + 0.059(14 - 6)]$$

$$\eta = -0.117 \text{V}$$

The overpotential at pH 7, 9, and 10 are $-0.058$, $0.06$, and $0.119$ V, respectively.

Figure 3.3 shows the oxygen overpotential dependence on pH. Assuming that the applied potential of platinum remains at 0.515 V vs. SCE, the oxygen reduction reaction occurs only when the pH is less than or equal to 8.

### 3.3.2 Low-field approximation

Another special case of the Butler-Volmer equation, Eq. (3.28), occurs when the overpotential is extremely small; under this condition, one can consider the value of $F\eta/RT$ to be small. In such a case, Eq. (3.28) can be approximated, based on the relations $[(e^x - e^{-x})/2 = \sinh x]$ and $[\sinh x = x$, when $x \to 0]$, to

$$i = i^o nF \frac{\eta}{RT}$$

(3.39)

The ratio of the overpotential to the current in the above equation is called the charge-transfer resistance. This equation adds more physical meaning to the exchange current density, $i^o$, and can be viewed as a parameter to estimate the resistance of an electrochemical (corrosion) reaction. A high value of the exchange current density implies high reaction rate, while a low exchange current density value indicates sluggish corrosion kinetics.
Based on low-field approximation, a simple procedure for the evaluation of corrosion currents and corrosion rates was developed in 1938 by Wagner and Traud [22]. Stern and Geary [23] and Stern [24,25] developed an experimental procedure for measuring the corrosion rates known as the linear polarization technique. This technique will be discussed in detail in Chapter 5.

**Example 3.4**

Calculate the hydrogen overpotential of an iron electrode and the corrosion current of iron for pH between 2 and 8. The potential of the iron electrode at unit hydrogen concentration (pH = 0), \( V = -0.75 \) V vs. SCE. The Tafel slope for the hydrogen evolution reaction is \( b_c = -0.12 \) V/decade. The exchange current density of hydrogen on iron \( i_o \) is \( 10^{-4} \) A/cm\(^2\). Assume that the corrosion potential is \( -0.5225 \) V vs. SHE.

**Solution:**

**Hydrogen overpotential:**

\[
2H^+ + 2e^- \rightarrow H_2, \quad \eta_{H^+|H_2} = 0.00 \text{V vs. SHE}
\]

\[
e_{eq,H^+|H_2} = -0.75 + \frac{RT}{2F} \log \left( \frac{a_{H_2}}{a_{H^+}} \right)
\]

\[
e_{eq,H^+|H_2} = \frac{0.059}{2} \log \left( \left( a_{H^+} \right)^2 \right)
\]

\[
e_{eq,H^+|H_2} = -0.059 \text{(pH)}
\]

\[
\eta_c = -0.75 - e_{eq,H^+|H_2}
\]

\[
\eta_c = -0.75 - \left( -0.059 \text{(pH)} \right)
\]

At a pH of 2, \( \eta_c = -0.75 + (0.059 \times 2) = -0.632 \) V

\( \eta_c \) is plotted as a function of pH in Fig. 3.4a.

**Corrosion current:**

Using Eq. (3.33),

\[
E_{corr} - e_{H^+|H_2} = b_c \log \left( \frac{i_{corr}}{i_o} \right)
\]

\[
\frac{E_{corr} - e_{H^+|H_2}}{b_c} = \log \left( \frac{i_{corr}}{i_o} \right)
\]

\[
i_{corr} = i_o \times 10^{(E_{corr} - e_{H^+|H_2})/b_c}
\]

For example, at pH = 2,

\[
i_{corr} = i_o \times 10^{(-0.5225 - (-0.059 \times 2))/ -0.12}
\]

\[
i_{corr} = 10^{-4} \times 10^{-0.4045/-0.12}
\]

\[
i_{corr} = 0.235 \text{A/cm}^2
\]

Similarly, the corrosion current for other pH values are calculated and plotted in Fig. 3.4b.
Example 3.5

The potential of platinum polarized in the cathodic direction in deaerated H₂SO₄ at a pH of 1.0 at 0.01 A/cm² is −0.334 V vs. SCE. At 0.10 A/cm² the potential is −0.364 V. Derive expression for the exchange current density, $i^{o}_{H_2}$ in terms of the overpotential and currents. Calculate $b_c$ (the Tafel constant) and $i^{o}_{H_2}$ (the exchange current density) for a discharge of H⁺ on platinum in this solution.
Solution:
The Tafel expressions for the two current densities are:

\[ \eta_{c1} = b_c \log \left( \frac{i_{1,H_2}}{i^0_{H_2}} \right) \]

\[ \eta_{c2} = b_c \log \left( \frac{i_{2,H_2}}{i^0_{H_2}} \right) \]

Next, one should estimate \( \eta_{c1} \) and \( i^0_{H_2} \). Because the two Tafel expressions for \( \eta_{c1} \) and \( \eta_{c2} \) are for the same reaction, the Tafel constant, \( b_c \), is the same. Exchange current density, \( i^0_{H_2} \), is calculated by eliminating \( b_c \) from the equations:

\[ \frac{(\eta_{c1})}{(\eta_{c2})} \log \left( \frac{i_{2,H_2}}{i^0_{H_2}} \right) = \log \left( \frac{i_{1,H_2}}{i^0_{H_2}} \right) \]

\[ \frac{(\eta_{c1})}{(\eta_{c2})} \log (i_{2,H_2}) - \frac{(\eta_{c1})}{(\eta_{c2})} \log (i^0_{H_2}) = \log (i_{1,H_2}) - \log (i^0_{H_2}) \]

\[ \frac{(\eta_{c1})}{(\eta_{c2})} \log (i_{2,H_2}) - \log (i_{1,H_2}) = \left[ \frac{(\eta_{c1})}{(\eta_{c2})} - 1 \right] \log (i^0_{H_2}) \]

\[ \log \left( \frac{i_{2,H_2}}{i_{1,H_2}} \right) = \log \left( \frac{i^0_{H_2}}{(\eta_{c1}/\eta_{c2}) - 1} \right) \]

The expression for the exchange current density is

\[ i^0_{H_2} = \left[ \frac{(\eta_{c1}/\eta_{c2})}{i_{1,H_2}} \right]^{1/[(\eta_{c1}/\eta_{c2}) - 1]} \]

The equilibrium potential of hydrogen ions in solution is estimated using the Nernst equation and can be expressed in terms of the pH of the solution.

\[ \eta = E - e_{eq} \]

\[ 2H^+ + 2e^- \rightarrow H_2, \quad e_{eq}^{H^+|H_2} = 0.00 \text{V vs. SHE} \]

\[ e_{eq,H^+|H_2} = 0.059 \text{(pH)} = -0.059 \text{V vs. SHE}, \text{ at pH} = 1; \text{ or } -0.059 - 0.241 = -0.300 \text{V vs. SCE} \]

The overpotentials are:

\[ \eta_{c1} = -0.334 - (-0.300) = -0.034 \text{V} \]

\[ \eta_{c2} = -0.364 - (-0.300) = -0.064 \text{V} \]

The exchange current density is calculated using the expression \( (A) \):

\[ i^0_{H_2} = \left[ \frac{0.1(-0.034/-0.064)}{0.01} \right]^{1/((-0.034/-0.064) - 1)} = 7.364 \times 10^{-4} \text{A/cm}^2 \]
Calculation of cathodic Tafel constant:

\[ \eta_{c1} = b_c \log \left( \frac{i_{1,H_2}}{i_{0,H_2}} \right) \]

\[ b_c = \frac{\eta_{c1}}{\log \left( \frac{i_{1,H_2}}{i_{0,H_2}} \right)} = \frac{-0.034}{0.01} = -0.030 \text{V/decade} \]

### 3.4 CONCENTRATION POLARIZATION

The previous discussion assumed that the reacting species concentration is always present in excess, and no limitations exist on the availability of the species (an ideal system). In real electrochemical reactions, the concentration of the species at the electrode continues to change as the reaction proceeds. This change in concentration is a result of the slow transport of species from the bulk solution to the surface of the electrode. Because the electrode potential is governed by the solution composition near the electrode surface, a change in the activity of species at the interface alters the equilibrium potential. Thus, the concentration polarization can be defined as shift of cell voltage due to concentration changes while current is passing. The overpotential developed as a result of such concentration polarization is called the diffusion overpotential ($\eta_d$), as discussed previously. Nernst’s law describes the diffusion overpotential phenomenon. If the activities of the oxidized and the reduced species at the start are $a_{M^+}$ and $a_M$, respectively, and change to $a'_{M^+}$ and $a'_M$ after the passage of current, then Nernst’s law allows the equilibrium potential at the start ($e_{eq}$) and after the passage of current ($e'_{eq}$) to be expressed as:

\[ e_{eq} = e^0 + \frac{RT}{nF} \ln \left( \frac{a_{M^+}}{a_M} \right) \]  

\[ e'_{eq} = e^0 + \frac{RT}{nF} \ln \left( \frac{a'_{M^+}}{a'_M} \right) \]  

and the concentration overpotential, $\eta_{conc}$, is given by

\[ \eta_{conc} = e'_{eq} - e_{eq} = \frac{RT}{nF} \ln \left( \frac{a'_{M^+} \cdot a_M}{a'_M \cdot a_{M^+}} \right) \]  

These relations are based on the fact that the potential loss due to charge-transfer reactions are negligible (the activation overpotential approaches zero). The diffusion overpotential is usually negative during cathodic processes and positive during anodic processes. The effects of concentration polarization are usually pronounced at high current densities, when a reaction species at the interface is consumed at a faster rate than it can be
replenished by transport from the bulk solution. As the current density increases, the polarization increases until the concentration of the species at the surface approaches zero. The current density at which this occurs is called the limiting current density, \( i_L \). Eq. (3.42) can now be written in terms of the limiting current density as \([7,19,20]\):

\[
\eta_{\text{conc}} = \frac{RT}{nF} \ln \left( \frac{i_L - i}{i_L} \right) \tag{3.43}
\]

where “\( i \)” is the current passing through the electrode when the surface concentration of the metal species is \( a_{M^+} \). The limiting current density is given by

\[
i_L = -\frac{DnFC_b}{\delta} \tag{3.44}
\]

where \( \delta \) is the diffusion layer thickness and \( D \) is the diffusion coefficient of the reacting species. Equation (3.43) also assumes that the linear part of the concentration profile is extrapolated to intersect the asymptotically approaching bulk value. Changes in the surface concentration of species can also occur due to chemical reactions.

### 3.5 RELEVANCE OF ELECTROCHEMICAL KINETICS TO CORROSION

The equilibrium of processes occurring at the electrode are disturbed when a net reaction occurs and produces current in the external circuit. The current induces a potential change and subsequently causes polarization of the electrode. The principle of charge conservation requires that the total rate of oxidation must be equal to the total rate of reduction for any corrosion process. To avoid the accumulation of charge on the electrode, the sum of anodic currents must equal the sum of cathodic currents. The electrochemical reaction at the anode is the oxidation (loss of electrons) of the metal, corrosion.

\[
M \rightarrow M^{n+} + ne^-
\]

At the cathode, electrons are gained. Examples of cathodic reactions are:

*Evolution of hydrogen from acidic, neutral, or alkaline solution:*

\[
2H^+ + 2e^- \rightarrow H_2 \text{ (acid solutions)}
\]
\[
2H_2O + 2e^- \rightarrow H_2 + 2OH^- \text{ (neutral and alkaline solutions)}
\]

*Evolution of dissolved oxygen in acid, neutral, or alkaline solution:*

\[
O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \text{ (acid solutions)}
\]
\[
O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \text{ (neutral and alkaline solutions)}
\]

*Reduction of oxidizer,*

\[
Fe^{3+} + e^- \rightarrow Fe^{2+}
\]
The concept of polarization in a corrosion cell can be explained by considering a simple galvanic cell, such as a Daniel cell, with copper and zinc electrodes. The Evans diagram of a Daniel cell shown in Fig. 3.5 is the basis for understanding the underlying corrosion process kinetics [26, 27].

The open circuit potential of copper in a copper ion solution and zinc in a zinc ion solution are represented as $e_{\text{eq,Cu}}$ and $e_{\text{eq,Zn}}$, respectively, in Fig. 3.5. The currents corresponding to the open circuit potentials are the exchange current densities of the electrode reactions. For such a cell, thermodynamics favors the reduction of copper and the oxidation of zinc and the criterion for a spontaneous reaction ($\Delta G = -nFE^0$) is valid.

Upon the polarization of either electrode, the cell potential moves along the oxidation and reduction curves as shown in Fig. 3.5. When the current through the cell is $i'$, the potential of the copper and zinc electrodes is $e_{1,\text{Cu}}$ and $e_{1,\text{Zn}}$, and each of the electrodes have been polarized by an amount of $(e_{\text{eq,Cu}} - e_{1,\text{Cu}})$ and $(e_{\text{eq,Zn}} - e_{1,\text{Zn}})$.

Upon further polarization, the anodic and cathodic curves intersect at a point where the potentials are the same ($E_{\text{corr}}$) and the external current is maximized. The electrode potentials at this point are numerically equal for copper and zinc and the current is $I_{\text{corr}}$. Physically, this point on Fig. 3.5 is attained when the load in the external circuit is extremely low or when the system is short circuited. Systems undergoing corrosion can be explained on a very similar basis. The measured output potential in a corroding system, often called the mixed potential or the corrosion potential ($E_{\text{corr}}$), is the potential at the intersection of the anodic and the cathodic polarization curves.

![Fig. 3.5 Schematic showing the anode and cathode polarization with the mixed potential (Evans diagram).](image)
The value of the current at the corrosion potential is called the corrosion current \( (I_{\text{corr}}) \) and can be used to calculate the rate at which the metal will corrode. To predict the corrosion current or the corrosion potential, we need information about the kinetics of the individual redox reactions, the standard electrode potentials, and the exchange current densities for a specific system.

The Evans diagram is also very useful in estimating the current required in the external circuit to stop the process of corrosion. If an external current is applied cathodically (negative current), the potential on the cathodic polarization line crosses the equilibrium potential of the anode and the anodic reaction is not thermodynamically feasible. Thus, the corrosion process stops. This process is the basis of cathodic protection and is discussed in Chapter 15.

### 3.6 CONSTRUCTION OF EVANS DIAGRAMS

Originally developed by Evans [26,27], the Evans diagram plots the potential vs. the log of the current density, generating a polarization diagram of a corroding metal. Evans diagrams are very useful in predicting the corrosion behavior of electrochemical systems. If polarization data is available, the Evans diagram can be used to estimate the exchange current densities of the anodic and cathodic reactions. When the exchange current densities and the equilibrium potentials of the anodic and cathodic reactions are known, Evans diagrams can be used to estimate the mixed potential (corrosion potential) of a system. A typical three-electrode electrochemical cell containing a working, counter, and reference electrode can be used to obtain polarization data [4–7].

Measurements are made by applying a current and monitoring the potential after a relaxation time and repeating the procedure for different anodic and cathodic currents. The experimental procedure for obtaining the polarization diagram of a corroding system requires the initial measurement of the open circuit potential of the system. The open circuit potential value falls between the equilibrium potentials of the anodic and cathodic reactions. When there is no current in the external circuit, an open circuit potential value is equal to the corrosion potential.

The second step in the procedure requires the working electrode to be anodically polarized, yielding one of the dashed lines shown in Fig. 3.6. The electrode is then cathodically polarized, and the other dashed line from Fig. 3.6 is obtained. The anodic polarization usually results in the oxidation of the metal species, while the reaction resulting from cathodic polarization depends on the medium. In an aerated solution, the oxygen reduction reaction may be the prime cathodic reaction, while, in the case of deaerated aqueous solutions, hydrogen reduction could be the dominant reaction. In Fig. 3.6, the redox reaction is represented by a general reaction:

\[
M^{n+} + ne^{-} \rightarrow M
\]
At significantly large overpotentials (>100 mV) the anodic and the cathodic polarization curves become linear. Linear extrapolation of the curves will yield a point of intersection at the corrosion potential with the corresponding current being the corrosion current. The experimental procedure above can also be performed potentiostatically using modern potentiostats that are capable of automatically handling the process.

As an alternative to generating an entire polarization diagram, we can use the exchange current densities and the equilibrium potentials of the anodic and cathodic reactions to estimate the corrosion potential and corrosion current by extrapolating the cathodic and anodic polarization lines of the corroding system. At the corrosion potential, the anodic and cathodic currents are equal. The schematic shown in Fig. 3.6 represents a case for which the anode and the cathode area are the same; once the corrosion current is known, the rate of deterioration of the electrode can be estimated. The accurate prediction of the corrosion (mixed) potential depends on the polarization behavior of the specific electrode.

Once the corrosion (mixed) potential is known, the estimation of the cathodic protection current is relatively simple; the cathodic Tafel line is extended until the ordinate reaches the anode equilibrium value. The current corresponding to that ordinate value is the minimum value of the external current that must be supplied to stop the corrosion process. For processes in which there are multiple species undergoing cathodic or anodic reactions, the resultant cathodic and anodic Tafel curves are calculated by adding the individual polarization curves within the respective potential range.

Fig. 3.6 Schematic showing the anodic and the cathodic parts of a corrosion reaction.
Case Study 3.1—Construction of the Evans Diagram for the Corrosion of Zinc

Construct the Evans diagram for the corrosion of zinc in a hydrochloric acid solution with a pH of 1 and a Zn\(^{2+}\) concentration of 10\(^{-5}\) M. The cathodic \((b_y = \partial \eta_c / \partial \log i)\) and anodic Tafel slope \((b_a = \partial \eta_a / \partial \log i)\) are -0.12 and 0.15 V/decade, respectively. The exchange current densities for the cathodic and anodic reactions are \(i_{o H_2} = 10^{-8}\) and \(i_{o Zn} = 2 \times 10^{-10}\) A/cm\(^2\), respectively.

(a) Calculate the corrosion potential and the corrosion current. Also evaluate the protection current required for the system. Assume that charge-transfer kinetics controls the reaction rate and that the high-field approximation applies.

(b) Calculate the corrosion potential when the pH of the solution is doubled, and the activity of the Zn\(^{2+}\) ion is squared.

Solution:

(a) According to Tafel kinetics and mixed potential theory:

\[
\eta_a = b_a \log \left( \frac{i_{corr}}{i_{o Zn}} \right) = E_{corr} - e_{eq,Zn^{2+} | Zn} \\
\eta_c = b_c \log \left( \frac{i_{corr}}{i_{o H_2}} \right) = E_{corr} - e_{eq,H^+ | H_2}
\]

The values for \(b_a, b_c, i_{o Zn}, \text{ and } i_{o H_2}\) are known. The equilibrium potential for the two reactions is estimated using the Nernst equation.

\[
e_{eq,Zn | Zn^{2+}} = e_{Zn^{2+} | Zn}^0 + \frac{0.059}{2} \log (a_{Zn^{2+}})
\]

\[
e_{eq,H^+ | H_2} = e_{H^+ | H_2}^0 + \frac{0.059}{2} \log (a_{H^+})^2
\]

At a pH of 1, the equilibrium hydrogen potential is:

\[
e_{eq,H^+ | H_2} = e_{H^+ | H_2}^0 + \frac{0.059}{2} \log (a_{H^+})^2 = 0.059 \text{ pH} = -0.059 \text{ V vs. SHE}
\]

Graphical construction:

(i) Refer to Fig. 3.7. Use a marker for each of these points \((i_{o Zn}, e_{eq,Zn})\) and \((i_{o H_2}, e_{eq,H_2})\) on an E vs. i, semilogarithmic graph with logarithmic values for the current.

(ii) From the points marked, draw straight lines with the slope \(b_c\) from \((i_{o H_2}, e_{eq,H_2})\) and \(b_a\) from \((i_{o Zn}, e_{eq,Zn})\).

(iii) The two straight lines intersect at the point \((I_{corr}, E_{corr})\), giving the corrosion current and corrosion potential.

(iv) Extend the cathodic polarization line until it reaches the anodic equilibrium potential on the ordinate. The corresponding current on the abscissa gives the value of the external current required to stop the corrosion process.

From Fig. 3.7, the following values are estimated:

\[
E_{corr} = 0.631 \text{ V}, \quad I_{corr} = 1.76 \times 10^{-6} \text{ A/cm}^2, \quad i_{prot} = 9.3 \times 10^{-5} \text{ A/cm}^2
\]
(b) When the pH of the system is doubled, and the activity of zinc is squared, the kinetic parameters remain the same but the equilibrium potential shifts based on the Nernst equation. Thus,

\[ \epsilon_{\text{eq,Zn}} = \epsilon_{\text{Zn}}^0 + \frac{0.059}{2} \log (a_{\text{Zn}^{2+}}) = -0.76 + \frac{0.0591}{2} \log (10^{-10}) = -1.055 \text{V} \]

From Fig. 3.8, the following values are estimated:

\[ E_{\text{corr}} = -0.33 \text{V}, \quad I_{\text{corr}} = 1.65 \times 10^{-6} \text{A/cm}^2, \quad i_{\text{prot}} = 0.13 \text{A/cm}^2 \]

Fig. 3.7 Evans diagram for zinc in hydrochloric acid.

Fig. 3.8 Evans diagram for zinc in hydrochloric acid, and the graph is drawn again as per the described procedure.
Case Study 3.2—Analytical Evaluation of the Corrosion Rate

The graphical construction performed in Case Study 3.1 may also be carried out in Case Study 3.2. Below is the derivation for the corrosion rate, $I_{\text{corr}}$. Rearranging Eq. (3.28), the Tafel kinetics for the anodic and the cathodic processes can be represented as:

\[
\eta_a = b_a \log \left( \frac{i_a}{i_{\text{Ox}}^o} \right) = E_{\text{corr}} - e_{\text{eq},\text{Ox}} \quad (3.45)
\]

\[
\eta_c = b_c \log \left( \frac{i_c}{i_{\text{R}}^o} \right) = E_{\text{corr}} - e_{\text{eq},\text{R}} \quad (3.46)
\]

Rewriting the equations for the corrosion potential, we obtain:

\[
E_{\text{corr}} = e_{\text{eq},\text{Ox}} + b_a \log \left( \frac{i_a}{i_{\text{Ox}}^o} \right) \quad (3.47)
\]

\[
E_{\text{corr}} = e_{\text{eq},\text{R}} + b_c \log \left( \frac{i_c}{i_{\text{R}}^o} \right)
\]

At the point where the anodic and cathodic polarization curves intersect, the anodic ($i_a$) and the cathodic ($i_c$) currents are equal to the corrosion current ($I_{\text{corr}}$), and so the set of Eq. (3.47) take the form:

\[
E_{\text{corr}} = e_{\text{eq},\text{Ox}} + b_a \log \left( \frac{I_{\text{corr}}}{i_{\text{Ox}}^o} \right) \quad (3.48)
\]

\[
E_{\text{corr}} = e_{\text{eq},\text{R}} + b_c \log \left( \frac{I_{\text{corr}}}{i_{\text{R}}^o} \right)
\]

where $I_{\text{corr}}$ and $E_{\text{corr}}$ are the only variables; the equilibrium potentials are calculated through the Nernst equation and the transfer coefficients are known parameters.

\[
e_{\text{eq},\text{Ox}} + b_a \left[ \log (I_{\text{corr}}) - \log (i_{\text{Ox}}^o) \right] = e_{\text{eq},\text{R}} + b_c \left[ \log (I_{\text{corr}}) - \log (i_{\text{R}}^o) \right]
\]

\[
e_{\text{eq},\text{R}} - e_{\text{eq},\text{Ox}} = b_a \left[ \log (I_{\text{corr}}) - \log (i_{\text{Ox}}^o) \right] - b_c \left[ \log (I_{\text{corr}}) - \log (i_{\text{R}}^o) \right]
\]

\[
E_{\text{cell}} = \log (I_{\text{corr}})(b_a - b_c) + b_c \log (i_{\text{R}}^o) - b_a \log (i_{\text{Ox}}^o)
\]

where $E_{\text{cell}} = e_{\text{eq},\text{R}} - e_{\text{eq},\text{Ox}}$.

Solving this equation and substituting Eq. (3.49) into either equation of Eq. (3.48), we obtain Eq. (3.50).

\[
I_{\text{corr}} = \exp \left[ \frac{(E_{\text{cell}} - b_c \log (i_{\text{R}}^o) + b_a \log (i_{\text{Ox}}^o))}{b_a - b_c} \right] \quad (3.49)
\]

\[
E_{\text{corr}} = \frac{b_a b_c (\log (i_{\text{Ox}}^o) - \log (i_{\text{R}}^o)) + (b_a e_{\text{eq},\text{R}} - b_c e_{\text{eq},\text{Ox}})}{b_a - b_c} \quad (3.50)
\]
Example 3.6
Determine the corrosion potential, the corrosion rate, and the protective current of zinc in 1 N hydrochloric acid. Assume that the entire zinc surface acts as a cathode, Tafel slopes are $b_a = 0.1$ V/decade and $b_c = -0.1$ V/decade, and the exchange current densities for zinc dissolution and for hydrogen evolution on zinc are $10^{-5}$ and $10^{-8}$ A/cm$^2$, respectively.

Additional information:

$$e^{0}_{Zn^{2+} | Zn} = -0.762 \text{V vs. SHE} \quad e^{0}_{H^{+} | H_2} = 0.00 \text{V vs. SHE}$$

$$i^{o}_{Zn} = 10^{-5} \text{A/cm}^2 \quad i^{o}_{H_2} = 10^{-8} \text{A/cm}^2$$

Solution:

Writing the Tafel equations for both the cathodic and anodic parts, we obtain:

$$E_{corr} = -0.762 = 0.1 \log \left( \frac{I_{corr}}{10^{-5}} \right)$$

$$E_{corr} - 0.0 = -0.1 \log \left( \frac{I_{corr}}{10^{-8}} \right)$$

These two equations can be solved simultaneously for $E_{corr}$ and $I_{corr}$.

Adding both equations, we obtain:

$$2E_{corr} + 0.762 = 0.1 \log \left( \frac{I_{corr} \cdot 10^{-8}}{10^{-5} I_{corr}} \right)$$

$$E_{corr} = -0.531 \text{V vs. SHE}$$

Substituting in the value of $E_{corr}$ in one of the Tafel equations, one obtains:

$$I_{corr} = 2.04 \times 10^{-3} \text{A/cm}^2$$

Because the protective potential is equal to the equilibrium potential or $E_{prot} = e_{eq, Zn^{2+} | Zn} = -0.762 \text{V vs. SHE}$, the overvoltage necessary to stop the corrosion is:

$$\eta_{prot} = E_{prot} - e_{eq, H^{+} | H_2} = -0.762 - 0.0 = -0.762 \text{V vs. SHE}.$$ 

The protective current at protective potential is calculated by using the Tafel equation:

$$-0.762 - 0.0 = -0.1 \log \left( \frac{i_{prot}}{10^{-8}} \right)$$

$$i_{prot} = 0.42 \text{A/cm}^2$$
Case Study 3.3

Calculate: (a) the corrosion rate of iron in an oxygen-free solution at a pH of 3.1, (b) the exchange current density for hydrogen evolution on iron, and (c) the cathodic current required to reduce the corrosion of iron to zero.

The concentration of the iron at the electrode interface is 0.02 M. The exchange current density for iron dissolution is \( i_0^{\text{Fe}} = 9 \times 10^{-7} \text{A/cm}^2 \) and the anodic slope \( b_a = 0.04 \text{V/decade} \); the corrosion potential of iron is \(-0.215 \text{V vs. RHE}\) and \( e^{\text{Fe}^{2+}|\text{Fe}} = -0.44 \text{V vs. SHE} \). For hydrogen evolution reaction (HER), the cathodic slope \( b_c = -0.12 \text{V/decade} \).

The required quantities can be obtained from an Evans diagram for the corrosion of iron in hydrogen-saturated, oxygen-free solution. Assume that charge-transfer kinetics controls the reaction rates and that the high-field approximation applies. In this example, iron corrodes by the electrochemical reaction producing iron ions at the anode:

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- 
\]

and hydrogen is reduced at the cathode:

\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2 
\]

According to mixed potential theory, any electrochemical reaction consists of partial reduction and oxidation reactions. In any redox reaction, such as the corrosion of a metal, there is no net accumulation of electric charge and the rate of the oxidation must equal the rate of reduction. At the intersection of the cathodic and anodic kinetic lines (see Fig. 3.8), the rates of oxidation and reductions are equal. This point represents the corrosion potential, \( E_{\text{corr}} \), and the corrosion current, \( I_{\text{corr}} \). At the corrosion potential, the rate of iron dissolution is equal to the rate of hydrogen evolution. Note in Fig. 3.8, these rates are expressed in terms of current density.

Solution:

According to the Butler-Volmer equation, we have:

\[
i = \dot{i} + \dot{i} - \dot{i} = i_0 \left\{ \exp \left( \frac{-\alpha_F \eta}{RT} \right) - \exp \left( \frac{\alpha_c \eta}{RT} \right) \right\} 
\]

where

\[
\eta_{\text{Fe}} = E_{\text{corr}} - e^{\text{Fe}^{2+}|\text{Fe}}; \ \eta_{\text{H}_2} = E_{\text{corr}} - e^{\text{H}^+|\text{H}_2}
\]

According to mixed potential theory:

\[
I_{\text{corr}} = i_{\text{Fe}} = i_{\text{H}_2}
\]

When the system departs very slightly from equilibrium

\[
(E_{\text{corr}} - e^{\text{Fe}^{2+}|\text{Fe}}) \gg 59 \text{mV}
\]

and

\[
(E_{\text{corr}} - e^{\text{H}^+|\text{H}_2}) \ll 59 \text{mV}
\]
The Butler-Volmer equation can be simplified for the anodic and cathodic reactions to:

\[ i_{H_2} = i_{H_2}^0 \exp \left( \frac{-\alpha_c nF}{RT} \eta_{H_2} \right) \]  

\[ i_{Fe} = i_{Fe}^0 \exp \left( \frac{\alpha_a nF}{RT} \eta_{Fe} \right) \]  

(3.51)

(3.52)

According to Eq. (3.52), the Tafel semilogarithm expressions are:

\[ \eta_{Fe} = -\frac{RT}{\alpha_a nF} \ln i_{Fe}^0 + \frac{RT}{\alpha_a nF} \ln i_{Fe} \]

\[ a_a = -2.3 \frac{RT}{\alpha_a nF} \log i_{Fe}^0 \quad \text{and} \quad b_a = 2.3 \frac{RT}{\alpha_a nF} \]

and

\[ \eta_{H_2} = \frac{RT}{\alpha_c nF} \ln i_{H_2}^0 - \frac{RT}{\alpha_c nF} \ln i_{H_2} \]

\[ a_c = 2.3 \frac{RT}{\alpha_c nF} \log i_{H_2}^0 \quad \text{and} \quad b_c = -2.3 \frac{RT}{\alpha_c nF} \]

(a) Calculation of corrosion rates:

\[ b_a = \frac{2.3RT}{\alpha_a nF} = \frac{\frac{d\eta_{Fe}}{d\log i}}{0.04 \text{ V/decade}} \]

\[ a_a = -\left( \frac{2.3RT}{\alpha_a nF} \right) \log i_{Fe}^0 = b_a \log i_{Fe}^0 \]

\[ = -0.04 \log (9 \times 10^{-7}) = 0.242 \text{ V} \]

\[ a_a = 0.242 \text{ V} \]

\[ e_{Fe^{2+} | Fe} = -0.44 + \frac{0.05916}{2} \log (0.02) = -0.490 \text{ V vs. SHE} \]

\[ e_{Fe^{2+} | Fe} \] is in standard hydrogen electrode (SHE) scale and it needs to be converted into RHE scale before calculating \( \eta \):

\[ e_{H^+ | H_2} = 0 - 0.05916 \text{ pH} = 0 - 0.05916 \times 3.1 = -0.183 \text{ V vs. SHE} \]

\[ e_{Fe^{2+} | Fe} = -0.490 - (-0.183) = -0.307 \text{ V vs. RHE} \]

\[ \eta_{Fe} = E_{\text{corr}} - e_{Fe^{2+} | Fe} = -0.215 - (-0.307) = 0.092 \text{ V} \]

\[ \eta_{Fe} = a_a + b_a \log i_{Fe} \]

\[ \log I_{\text{corr}} = -3.75 \]

\[ I_{\text{corr}} = 1.78 \times 10^{-4} \text{ A/cm}^2 \]

(b) Calculation of exchange current density for the hydrogen evolution reaction on iron:

\[ \eta_{H_2} = a_c + b_c \log i_{H_2} \]

\[ b_c = \frac{2.3RT}{\alpha_c nF} = \frac{d\eta_{H_2}}{d\log i} = -0.12 \text{ V} \]
(c) Calculation of protection current:
To stop the corrosion of Fe, it is necessary to shift the iron corrosion to its equilibrium potential value $e_{\text{eq}, \text{Fe}^{2+} | \text{Fe}}$. Thus, $E_{\text{prot}} = e_{\text{eq}, \text{Fe}^{2+} | \text{Fe}} = -0.490 \text{ V vs. SHE}$. At this potential, the corrosion reaction is reversed and the overvoltage for iron dissolution is equal to zero.

$$
\eta_{\text{prot}} = e_{\text{Fe}^{2+} | \text{Fe}} - e_{\text{H}^{+} | \text{H}_2} ; \ \eta_{\text{Fe}} = 0
$$

$$
\eta_{\text{prot}} = -0.490 + 0.183 = -0.307 \text{ V}
$$

The cathodic current required to shift the iron electrode potential to its reversible value is calculated using the Tafel equation or:

$$
\log i_{\text{cathode}} = \left( \eta_{\text{H}_2} - a_c \right)/b_c = \left( -0.307 + 0.665 \right)/(-0.12) = -2.98;
$$

$$
i_{\text{cathode}}(i_{\text{prot}}) = 0.001 \text{ A/cm}^2
$$

As shown in Fig. 3.9, to eliminate corrosion a cathodic current of 0.001 A/cm$^2$ should be applied to an iron electrode to shift the Fe$|\text{Fe}^{2+}$ electrode potential to $-0.490 \text{ V vs. SHE}$, where the electrode is at equilibrium.

![Evans diagram](image-url)

**Fig. 3.9** Evans diagram for the iron dissolution in hydrogen-saturated oxygen-free solution of pH = 3.1.
Example 3.7 Iron corrosion in oxygen-saturated solution and evaluation of impressed current-cathodic protection system.

(a) Consider iron in a solution with a pH of 7 saturated with oxygen and a partial pressure of oxygen, \( P_{O_2} = 1 \text{ atm} \). Calculate the corrosion current and the corrosion potential.

(b) Estimate the protection current required to reduce the corrosion current to zero:

Additional information:

\[
\begin{align*}
[\text{Fe}^{2+}] &= 0.7 \text{ M} \quad P_{O_2} = 1 \text{ atm} \\
\eta_a &= 0.08 \text{ V/decade} \quad \eta_c = -0.11 \text{ V/decade} \\
\eta_{Fe}^0 &= 10^{-5} \text{ A/cm}^2 \quad \eta_{OH}^0 = 10^{-6} \text{ A/cm}^2
\end{align*}
\]

Solution:

Calculating the potentials:

\[
\begin{align*}
2\text{Fe}^{2+} + 4e^- &\rightarrow 2\text{Fe}, \quad e_{\text{Fe}^{2+}|\text{Fe}}^0 = -0.440 \text{ V vs. SHE} \\
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- &\rightarrow 4\text{OH}^-, \quad e_{\text{O}_2|\text{OH}^-}^0 = 0.401 \text{ V vs. SHE}
\end{align*}
\]

\[
e_{\text{eq, O}_2|\text{OH}^-} = e_{\text{O}_2|\text{OH}^-}^0 - 2.303 \frac{RT}{nF} \log \left( \frac{(a_{\text{OH}^-})^4}{P_{O_2}} \right)
\]

\[
e_{\text{eq, O}_2|\text{OH}^-} = 0.401 + 0.059(14 - 7)
\]

\[
e_{\text{eq, O}_2|\text{OH}^-} = 0.814 \text{ V vs. SHE}
\]

\[
e_{\text{Fe}^{2+}|\text{Fe}} = e_{\text{Fe}^{2+}|\text{Fe}}^0 - 2.303 \frac{RT}{nF} \log \left( \frac{a_{\text{Fe}}}{(a_{\text{Fe}^{2+}})^2} \right)
\]

\[
e_{\text{Fe}^{2+}|\text{Fe}} = -0.440 - \frac{0.059}{4} \log \left( \frac{1}{(0.7)^2} \right)
\]

\[
e_{\text{Fe}^{2+}|\text{Fe}} = -0.445 \text{ V vs. SHE}
\]

Calculation of \( E_{\text{corr}} \) and \( I_{\text{corr}} \):

\[
\eta = b \log \left( \frac{i}{i^0} \right)
\]

\[
\eta_c = b_c \log (I_{\text{corr}}) - b_c \log (i_{\text{OH}^-}^0)
\]

\[
\eta_a = b_a \log (I_{\text{corr}}) - b_a \log (i_{\text{Fe}}^0)
\]

\[
E_{\text{corr}} = e_{\text{O}_2|\text{OH}^-} + b_c \log \left( \frac{I_{\text{corr}}}{i_{\text{OH}^-}^0} \right)
\]

\[
E_{\text{corr}} = e_{\text{eq, Fe}^{2+}|\text{Fe}} + b_a \log \left( \frac{I_{\text{corr}}}{i_{\text{Fe}}^0} \right)
\]
$I_{\text{corr}}$ and $E_{\text{corr}}$ are calculated using Eqs (3.49) and (3.50):

$$\log(I_{\text{corr}}) = \left[ \frac{(E_{\text{cell}} - b_a \log(i_{\text{OH}}^0) + b_a \log(i_{\text{Fe}}^0))}{(b_a - b_c)} \right]$$

$$I_{\text{corr}} = 10 \left[ (E_{\text{cell}} - b_a \log(i_{\text{OH}}^0) + b_a \log(i_{\text{Fe}}^0)/(b_a - b_c) \right]$$

$$= 10 \left[ (1.259 - (-0.11) \log(10^{-6}) + 0.08 \log(10^{-5}))/(-0.11) \right]$$

$$I_{\text{corr}} = 11.2 \text{ A/cm}^2$$

Using the analytical solution for the corrosion potential, Eq. (3.50),

$$E_{\text{corr}} = \frac{b_a b_c (\log(i_{\text{Fe}}^0) - \log(i_{\text{OH}}^0) + (b_a e_{\text{eq},O}_2|\text{OH}^- - b_c e_{\text{eq},\text{Fe}^{2+}}|\text{Fe})}{(b_a - b_c)}$$

$$E_{\text{corr}} = \frac{(0.08 \times (-0.11) \log(10^{-5}) - \log(10^{-6})) + (0.08 \times 0.814) - (-0.11) \times -0.45}{(0.08 - (-0.11))}$$

$$E_{\text{corr}} = 0.039 \text{ V vs. SHE}$$

Shifting the iron corrosion potential to the equilibrium potential value will stop the corrosion of Fe, $E_{\text{prot}} = e_{\text{eq},\text{Fe}^{2+}}|\text{Fe} = -0.45 \text{ V vs.SHE}$. To reverse the corrosion reaction, the overvoltage for iron dissolution must be zero, $\eta_{\text{Fe}} = 0$;

$$\eta_{\text{prot}} = E_{\text{prot}} - e_{\text{eq},\text{OH}^-}; \eta_{\text{Fe}} = 0$$

$$\eta_{\text{prot}} = -1.259 \text{ V vs. SHE}$$

The cathodic current that is applied to the iron electrode to shift the iron electrode potential to its reversible value is calculated using the Tafel equation:

$$\log(i_{\text{prot}}) = \frac{\eta_{\text{prot}} - a_c}{b_c}$$

$$i_{\text{prot}} = 10(\eta_{\text{prot}} - a_c)/b_c$$

According to Eqs. (3.31a) and (3.31b),

$$a_c = 2.3 \frac{RT}{a_c nF} \log i_{c}^0$$

and

$$b_c = -2.3 \frac{RT}{a_c nF}$$

or

$$a_c = -b_c \log(i_{c}^0)$$

$$a_c = 0.11 \log(10^{-6})$$

$$a_c = -0.66 \text{ V vs.SHE}$$

$$i_{\text{prot}} = 10(-1.259 + 0.66)/-0.11$$

$$i_{\text{prot}} = 2.79 \times 10^{5} \text{ A/cm}^2$$
A cathodic current of $3.03 \times 10^5 \text{ A/cm}^2$ should be applied to the iron electrode to shift the Fe/Fe$^{2+}$ electrode potential to its reversible value of $-0.449 \text{ V vs. SHE}$, where the electrode is at equilibrium as shown in Fig. 3.10. The effect of electrode material and solution composition on oxygen overpotential is given in Table 3.3.

### 3.7 EFFECTS OF POLARIZATION BEHAVIOR ON THE CORROSION RATE

The mixed potential depends on the polarization behavior of the anodic and cathodic reactions. More precisely, specific parameters determine whether the mixed potential is close to the equilibrium value of the anode reaction or the cathode reaction. These parameters include the exchange current density and anodic and cathodic reaction transfer coefficients, which determine the Tafel slope. Based on these criteria, when the cathode is a highly polarizable electrode in comparison to the anode or when the Tafel slope for the cathodic reaction is much larger than the anodic reaction, the system is said to be cathodically controlled. In such a case, the corrosion potential of the system is very close to the anode equilibrium potential and is represented in Fig. 3.11a.

Conversely, when the anode is highly polarized in comparison to the cathode, the mixed potential lies close to the cathode equilibrium potential and such systems are anodically controlled. This type of corroding system is described in Fig. 3.11b.

A corroding system may be anodically or cathodically controlled based on the polarization of the corroding electrode in the specific medium. In some cases, the electrolyte resistance is so high that the electrodes will not be sufficiently polarized. In these cases, the corrosion current is controlled by the ohmic resistance in the solution.
Example 3.8—Effects of Polarization Behavior on the Corrosion Rate

For the following reactions:

\[
2\text{H}^{+} + 2\text{e}^- \rightarrow \text{H}_2 (\text{HydrogenEvolution})
\]
\[
\text{M} \rightarrow \text{M}^{2+} + 2\text{e}^- (\text{MetalDissolution})
\]

show that

(a) The corrosion current can be expressed as:

\[
I_{corr} = \left\{ \left( \frac{i_0^M}{i_0^H_2} \right)^{b_i} \cdot \exp \left( 2.303 \left( \epsilon_{\text{eq},\text{H}^{+} | \text{H}_2} - \epsilon_{\text{eq},\text{M}^{2+} | \text{M}} \right) \right) \right\}^{1/(b_i - b_c)}
\]

Fig. 3.11 Effect of the polarization curve on the mixed potential of a corroding system: (a) cathodically controlled, (b) anodically controlled.
(b) When the exchange current densities for both the reactions are equal and the ratio of the transfer coefficients is 1/2 (i.e., \( \alpha_a = \alpha_c = 1/2 \)), the corrosion potential is given by

\[
E_{\text{corr}} = \frac{E_{\text{eq,M}^2+|M} + 2E_{\text{eq,H}^+|H_2}}{3}
\]

**Solution:**

(a) The anodic and the cathodic processes occur according to the Tafel equations and intersect at the corrosion potential. Therefore,

\[
\eta_a = b_a \log \left( \frac{I_{\text{corr}}}{i^0_M} \right) = E_{\text{corr}} - e_{\text{eq,M}^2+|M}
\]

\[
\eta_c = b_c \log \left( \frac{I_{\text{corr}}}{i^0_{H_2}} \right) = E_{\text{corr}} - e_{\text{eq,H}^+|H_2}
\]

Eliminating \( E_{\text{corr}} \), we obtain:

\[
-e_{\text{eq,M}^2+|M} + e_{\text{eq,H}^+|H_2} = \log \left( \left( \frac{I_{\text{corr}}}{i^0_M} \right)^{b_a} \left( \frac{I_{\text{corr}}}{i^0_{H_2}} \right)^{-b_c} \right)
\]

\[
-e_{\text{eq,M}^2+|M} + e_{\text{eq,H}^+|H_2} = \log \left( \left( \frac{i^0_M}{i^0_{H_2}} \right)^{b_a - b_c} \left( \frac{i^0_M}{i^0_{H_2}} \right)^{-b_c} \right)
\]

\[
I_{\text{corr}} = \left\{ \left( \frac{i^0_M}{i^0_{H_2}} \right)^{b_a - b_c} \exp \left( 2.303 \left( E_{\text{eq,H}^+|H_2} - E_{\text{eq,M}^2+|M} \right) \right) \right\}^{\frac{1}{b_a - b_c}}
\]

If \( \left( \frac{\alpha_a}{\alpha_c} = \frac{1}{2} \right) \), then \( \left( \frac{b_a}{b_c} = -2 \right) \); \( b_c = -2.3 \frac{RT}{\alpha_c nF}, b_a = -2.3 \frac{RT}{\alpha_a nF} \).

Because \( \eta_a = b_a \log \left( \frac{I_{\text{corr}}}{i^0_M} \right) = E_{\text{corr}} - e_{\text{eq,M}^2+|M}; \eta_c = b_c \log \left( \frac{I_{\text{corr}}}{i^0_{H_2}} \right) = E_{\text{corr}} - e_{\text{eq,H}^+|H_2} \)

Rearranging the equations, we obtain:

\[
\frac{E_{\text{corr}} - e_{\text{eq,M}^2+|M}}{b_a} = \log \left( \frac{I_{\text{corr}}}{i^0_M} \right)
\]

\[
\frac{E_{\text{corr}} - e_{\text{eq,H}^+|H_2}}{b_c} = \log \left( \frac{I_{\text{corr}}}{i^0_{H_2}} \right)
\]

Because the exchange current densities are equal, \( i^0_M = i^0_{H_2} \), the above equations become

\[
E_{\text{corr}} - e_{\text{eq,M}^2+|M} = \frac{b_a}{b_c} \left( E_{\text{corr}} - e_{\text{eq,H}^+|H_2} \right)
\]

from which

\[
E_{\text{corr}} = \frac{e_{\text{eq,M}^2+|M} + 2e_{\text{eq,H}^+|H_2}}{3}
\]
3.8 EFFECTS OF MASS TRANSFER ON ELECTRODE KINETICS

Under well-stirred conditions, when the currents are kept low enough for the concentration gradients in the electrolyte to be minimized, and the concentration at the electrode-electrolyte interface and the bulk do not vary significantly, Eq. (3.28) is valid. In real-time electrochemical applications, appreciable concentration gradients between the bulk and the interface always exist, and one often desires a rate expression that includes the concentration terms. At equilibrium, the rates of the forward and backward reactions are equal, and Eqs. (3.21a) and (3.21b) can be written as:

\[ i_c = i_a = i^0 \]  

(3.24)

and

\[ Fk_c^0 C_o \exp \left( \frac{-\alpha_c F (E - e_{eq})}{RT} \right) = Fk_a^0 C_R \exp \left( \frac{\alpha_a F (E - e_{eq})}{RT} \right) \]  

(3.53)

At equilibrium, the bulk concentration and the surface concentration are the same, and Eq. (3.53) can be written as:

\[ i^0 = Fk_a^b C_R exp \left( \frac{-\alpha_c F (e_{eq} - e^0)}{RT} \right) = Fk_a^b C_R \exp \left( \frac{\alpha_a F (e_{eq} - e^0)}{RT} \right) \]  

(3.54)

where \( C_o^b \) and \( C_R^b \) are the concentrations of the oxidized species and reduced species in the bulk of the electrolyte at equilibrium. The current is the difference between the rates of the forward and the reverse reactions, which yields:

\[ i = Fk_c^0 C_O \exp \left( \frac{-\alpha_c F (E - e_{eq})}{RT} \right) - Fk_a^0 C_R \exp \left( \frac{\alpha_a F (E - e_{eq})}{RT} \right) \]  

(3.55)

Combining Eqs. (3.54) and (3.55), we obtain:

\[ \frac{i}{i^0} = \frac{Fk_c^0 C_O \exp \left( \frac{-\alpha_c F (E - e_{eq})}{RT} \right)}{Fk_a^b C_R \exp \left( \frac{-\alpha_c F (e_{eq} - e^0)}{RT} \right)} \]  

(3.56)

Upon rearranging, the concentration dependent Butler-Volmer equation is obtained.

\[ i = i^0 \left\{ \frac{C_O}{C_R} \exp \left( \frac{-\alpha_c F (E - e_{eq})}{RT} \right) - \frac{C_R}{C_R^b} \exp \left( \frac{\alpha_a F (E - e_{eq})}{RT} \right) \right\} \]  

(3.57)

When there is no significant concentration gradient between the interface and the bulk, \( C_R = C_R^b \) and \( C_O = C_O^b \), Eq. (3.57) takes the form of Eq. (3.27). Based on the definition of limiting current (concentration at the interface is zero), one can evaluate the ratio of the concentration at the surface and the bulk to be:

\[ \frac{C_R}{C_R^b} = 1 - \frac{i}{i_s,L} \]  

(3.58a)
\[
\frac{C_{OB}}{C_{O}} = 1 - \frac{i}{i_{c,L}}
\]  
(3.58b)

where \(i_{a,L}\) and \(i_{c,L}\) are the anodic and cathodic limiting current densities, respectively. Thus, Eq. (3.57) may be more conveniently written in terms of limiting current density as:

\[
i = i^0 \left\{ \left( 1 - \frac{i}{i_{c,L}} \right) \exp \left( \frac{-\alpha_F(E - e_{eq})}{RT} \right) - \left( 1 - \frac{i}{i_{a,L}} \right) \exp \left( \frac{\alpha_F(E - e_{eq})}{RT} \right) \right\} \quad (3.59)
\]

The effect of mass transfer on electrode kinetics is shown in Fig. 3.12. Many useful kinetic rate expressions based on Tafel conditions, mass transport limitations can be developed from Eq. (3.59). Prediction of mass transfer effects may be useful in corrosion systems depending on the system’s corrosion conditions. The mass transport limitations in corrosion systems may alter the mixed potential of a corroding system. Under Tafel conditions (anodic or cathodic), Eq. (3.59) can be written as:

\[
i_a = -i^0 \left( 1 - \frac{i}{i_{a,L}} \right) \exp \left( \frac{\alpha_F(E - e_{eq})}{RT} \right)
\]

\[
i_c = i^0 \left( 1 - \frac{i}{i_{c,L}} \right) \exp \left( -\frac{\alpha_F(E - e_{eq})}{RT} \right)
\]  
(3.60)

### 3.8.1 Diffusion-limited corrosion rate

The relationship between the potential and the logarithmic current density is not always linear (Tafel expression). In the case of a reacting species that is diffusion controlled, the logarithm of current density does not increase proportionally beyond a certain value of

![Fig. 3.12 Effect of concentration polarization.](image)
the overpotential. In such a case, the Evans diagram looks qualitatively like those in Fig. 3.13a or b, which represent a cathodically diffusion-limited system and an anodically diffusion-limited process (both the anodic and cathodic currents can be diffusion limited). The mixed potential in a diffusion-limited process is denoted by $E_{\text{corr}}$, while the mixed potential without diffusion limitations is represented by $E'_{\text{corr}}$; the corrosion currents for cases with and without diffusion limitations are denoted in a similar manner. Due to the

Fig. 3.13 Influence of diffusion-controlled polarization curves on the mixed potential of corroding systems: (a) cathodic diffusion control and (b) anodic diffusion control.
system’s departure from linearity, the corrosion current and thus the corrosion rate for a diffusion-controlled system is lower than that of a system with linear kinetics (as shown by the dotted lines). Equation (3.32) for a diffusion-limited case would be:

\[ \eta = b_c \log \frac{i}{i_o 1/C_0 i_c,L/C_{18}/C_{19}} \] (3.61)

When the limiting current density, \( i_{c,L} \), is large, Eq. (3.61) reduces to Eq. (3.32). Diffusion limitations can be suppressed by vigorously stirring the electrolyte solution. The mixing reduces the concentration gradients and increases species availability at the interface, thereby allowing the reactions to take place at a higher rate.

### 3.8.2 Rotating disk electrode

The rotating disk electrode is one of the most popular convective electrode systems and is widely used for research purposes to study the kinetics of electrochemical reactions. This is because it provides uniform concentration gradients along the electrode surface during electrochemical processes. The frequency of electrode rotation is controlled to adjust the extent of convection in the system. The hydrodynamics of the rotating disk electrode have been studied extensively [28–37] and an important result is the Levich equation:

\[ i_L = 0.62nF D_o^{2/3} \omega^{1/2} \nu^{-1/6} C_b \] (3.62)

where \( i_L \) is the current density that would be obtained in the limiting case when the concentration of the reaction species at the surface of the electrode is equal to zero. The term \( \omega \) is the angular velocity, \( C_b \) is the concentration of the species in the bulk (far from the rotating disk electrode surface), \( \nu \) is the kinematic viscosity, and \( D_o \) is the diffusivity of the species in the electrolyte. The Levich equation [28] takes into account both the rate of diffusion across the stagnant layer and the complex flow pattern near the rotating disk electrode surface. In particular, the Levich equation gives the peak current observed in rotating disk voltammetry. The limiting current thus obtained may be relevant to corrosion in that it changes the mixed potential and corrosion current, depending on the rotation speed. As shown in Fig. 3.14, increased angular velocity of the rotating disk electrode increases the corrosion rate to the point where the cathodic limiting current reaches the intersection of the cathodic and anodic polarization curves for the Tafel case. When the cathodic limiting current is greater than the Tafel case intersection, the effect of velocity does not affect the corrosion potential or the corrosion current. The cathodic polarization in Fig. 3.14 is diffusion limited, while the anodic polarization is of the Tafel type, without concentration limitations.
Case Study 3.4—Effect of Limiting Current Density on the Corrosion Potential and Corrosion Current

For a system $10^{-3}$ M Cr$^{3+}$ in hydrochloric acid at a pH of 1:

(a) Determine the corrosion current and potential

(b) Evaluate the corrosion current and potential if the mass transport limitation for a hydrogen reaction limits the maximum current to $10^{-5}$ A/cm$^2$.

(c) How would the corrosion potential and current change if the limiting current density for the hydrogen evolution reaction was $10^{-3}$ A/cm$^2$?

(d) Plot the Evans diagram for the three cases.

The values of the cathodic ($b_c$) and anodic ($b_a$) Tafel slopes are $-0.10$ V/decade and $0.12$ V/decade, respectively. The exchange current densities for both the anodic and cathodic reactions are given to be $10^{-6}$ and $10^{-8}$ A/cm$^2$.

Additional information:

\[ b_a = 0.12 \text{ V/decade} \quad b_c = -0.1 \text{ V/decade} \]

\[ i_{\text{Cr}^{2+}} = 10^{-6} \text{ A/cm}^2 \quad i_{\text{H}_2} = 10^{-8} \text{ A/cm}^2 \]

Solution:

The half-cell equilibrium potentials are calculated based on the Nernst equation:

\[ \epsilon_{\text{eq,Cr}^{2+}} = \epsilon_{\text{Cr}^{3+}|\text{Cr}^{2+}} + \frac{0.059}{3} \log \left( a_{\text{Cr}^{3+}} \right) = -0.744 + \frac{0.059}{3} \log \left( 10^{-3} \right) = -0.803 \text{ V vs. SHE} \]

\[ \epsilon_{\text{eq,H}^{+}|\text{H}_2} = \epsilon_{\text{H}^{+}|\text{H}_2} + \frac{0.059}{3} \log \left( a_{\text{H}^{+}} \right)^3 = -0.059 \log (pH) = -0.059 \text{ V vs. SHE} \]

(a) Writing the Tafel equations for both the cathode and anode, we obtain:
\[ E_{\text{corr}} - (-0.059) = -0.1 \log \left( \frac{I_{\text{corr}}}{10^{-8}} \right) \]

\[ E_{\text{corr}} - (-0.803) = 0.12 \log \left( \frac{I_{\text{corr}}}{10^{-6}} \right) \]

Solving the above equations

\[ E_{\text{corr}} = -0.506 \text{ V vs. SHE} \]

\[ I_{\text{corr}} = 2.97 \times 10^{-4} \text{ A/cm}^2. \]

(b) When the cathodic current is limited by diffusion to a maximum of \( 10^{-5} \text{ A/cm}^2 \) then the mixed potential will be on the anodic line where the current is \( 10^{-5} \text{ A/cm}^2 \) (\( I_{\text{corr}} = 10^{-5} \text{ A/cm}^2 \)).

Thus, the mixed potential in this case would be:

\[ E_{\text{corr}} - (-0.803) = 0.12 \log \left( \frac{10^{-5}}{10^{-6}} \right); E_{\text{corr}} = -0.683 \text{ V vs. SHE} \]

(c) When the cathodic limiting current density is \( 10^{-3} \text{ A/cm}^2 \), more than when there was no diffusion limitation (part a), then the effect of limiting current density does not influence the corrosion current or the corrosion potential and so the analysis of part (a) is not affected and the results are the same:

\[ E_{\text{corr}} = -0.506 \text{ V vs. SHE} \]

\[ I_{\text{corr}} = 2.97 \times 10^{-4} \text{ A/cm}^2 \]

The Evans diagrams for the three cases are shown in Fig. 3.15a–c.

(d) The effect of the limiting current density on the corrosion potential and corrosion current is shown in Fig. 3.15a and b.

\[ \text{Fig. 3.15} \text{ Evans diagram showing the effect of limiting current density on the corrosion potential and corrosion current.} \]
Case Study 3.5—The Effect of Rotation Speed on the Corrosion Potential

In a rotating disk system of iron in sulfuric acid maintained at a pH of 1, the limiting cathodic current density due to the evolution of hydrogen changes with rotation speed. As a result, the corrosion potential of the system also changes. (a) Plot the modified Evans diagram, showing the effect of limiting current on the corrosion potential and corrosion current for various rotation speeds. Show how the corrosion potential varies as a function of the rotating speed and evaluate the critical velocity.
beyond which the corrosion potential of this system equals the corrosion potential of a similar system with no diffusion limitations.

**Additional information:**
The cathodic and anodic reaction parameters are $\frac{\partial \eta_c}{\partial \log i} = -0.05$ V/decade, $\frac{\partial \eta_a}{\partial \log i} = 0.05$ V/decade, $i_{H_2}^0 = 10^{-8}$ A/cm$^2$, $i_{Fe}^0 = 10^{-6}$ A/cm$^2$. Assume the concentration of Fe$^{2+}$ in the system to be equal to 0.3 M, $D_o = 10^{-12}$ m$^2$/s, $\nu = 1$ cP.

**Solution:**
The half-cell equilibrium potentials are calculated based on the Nernst equation.

$$e^{eq,Fe^{2+}}_{|Fe} = e^{0}_{Fe^{2+}}_{|Fe} + 0.059 \cdot \log(a_{Fe^{2+}}) = -0.440 + 0.059 \cdot \log(0.3) = -0.455 \text{V vs. SHE}$$

$$e^{eq,H^+}_{|H_2} = e^{0}_{H^+}_{|H_2} + 0.059 \cdot \log(a_{H^+})^2 = -0.059 (\text{pH}) = -0.059 \text{V vs. SHE}$$

The corrosion potential and corrosion current when there are no diffusion limitations or the rotating speed tends to infinity are calculated by solving the anodic and cathodic Tafel equations. Writing the Tafel equations for both the cathodic and anodic parts, we obtain:

$$E_{corr} + 0.059 = -0.05 \log \left( \frac{I_{corr}}{10^{-8}} \right)$$

$$E_{corr} + 0.4554 = 0.05 \log \left( \frac{I_{corr}}{10^{-6}} \right)$$

Solving the above equations, we obtain:

$$E_{corr} = -0.307 \text{V vs. SHE}$$

$$I_{corr} = 9.21 \times 10^{-4} \text{A/cm}^2$$

The limiting current density is then calculated as a function of rotation speed using the Levich equation. From Eq. (3.62), we obtain:

$$i_L = 0.62nFD_o^{2/3} \omega^{1/2} \nu^{-1/6}$$

$C_b = 0.62 \times 2 \times 96487 \times (10^{-12})^{2/3} \omega^{1/2}(10^{-3})^{-1/6} \times 0.3 \times 10^3 \text{A/cm}^2$

$$i_L = 1.135 \times 10^{-4} \omega^{1/2} \text{A/cm}^2$$

Rewriting the Tafel equations and considering the cathodic diffusion limitations, we obtain using Eq. (3.61):

$$E_{corr} - (-0.059) = -0.05 \log \frac{I_{corr}}{10^{-8}} \left( 1 - \frac{I_{corr}}{i_L} \right)$$

$$E_{corr} - (-0.4554) = 0.05 \log \left( \frac{I_{corr}}{10^{-6}} \right)$$

Utilizing the expression for the cathodic limiting current density as a function of the rotation speed, the Tafel equations take the form:

$$E_{corr} + 0.059 = -0.05 \log \frac{I_{corr}}{10^{-8}} \left( 1 - \frac{2I_{corr}}{1.135 \times 10^{-4} \omega^{1/2}} \right)$$
Solving these two equations for a particular value of angular velocity, we obtain the corrosion potential and the corrosion current. Figure 3.16 shows the Evans diagram plotted for various angular velocities. As noted from the plot, below 600 rpm the anodic and the cathodic slopes intersect closer to the equilibrium potential of iron, while beyond 600 rpm, no matter how much the rotation speed is increased, the corrosion potential is always equal to the corrosion potential of the system when there are no diffusion limitations (shown in the cathodic dark line).

The effect of rotation speed on the corrosion potential of a system is shown in Fig. 3.17. This figure shows that beyond about 600 rpm, the corrosion potential remains the same.
Case Study 3.6—Effect of Rotational Speed on Corrosion Potential

Consider iron immersed in an aerated corrosive solution saturated with oxygen. The oxygen reduction in this system is diffusion controlled. Table 3.4 shows the variation of the limiting current of oxygen with the velocity of the electrolyte.

Table 3.4 Limiting Cathodic Current Data as a Function of Electrolyte Velocity

<table>
<thead>
<tr>
<th>Electrolyte Velocity (m/s)</th>
<th>Limiting Current (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0(1)</td>
<td>0.001</td>
</tr>
<tr>
<td>10(2)</td>
<td>0.010</td>
</tr>
<tr>
<td>20(3)</td>
<td>0.100</td>
</tr>
<tr>
<td>30(4)</td>
<td>1.000</td>
</tr>
<tr>
<td>40(5)</td>
<td>10.00</td>
</tr>
</tbody>
</table>

(a) Construct the cathodic and anodic Tafel plots for the above system under each case. Also, calculate the corrosion current and corrosion potential for each case. Plot the corrosion current vs. velocity, and explain the effect of the electrolyte velocity.

(b) To protect the above system, a sacrificial Zn–Mn alloy with an equilibrium potential of −1.0 V vs. SHE is coupled to the system. Estimate the galvanic current, corrosion potential, and corrosion current of the system for the above plots when the sacrificial anode is coupled to iron.

Given:

\[ b_a = 0.1, \quad b_c = -0.1 \quad P_{O_2} = 1\, \text{atm}, \quad \left[ \text{Fe}^{2+} \right] = 0.5\, \text{M}, \quad \text{pH} = 10 \]

\[ i_{O_2|OH^-}^0 = 10^{-7} \, \text{A/cm}^2 \quad i_{\text{Fe}^{+2}|\text{Fe}}^0 = 10^{-5} \, \text{A/cm}^2 \quad e_{\text{eq,Fe}^{+2}|\text{Fe}} = -0.4606 \, \text{V vs. SHE} \]

\[ i_{\text{Zn-Mn} \text{ anode}}^0 = 10^{-5} \, \text{A/cm}^2 \quad e_{\text{eq, Zn|Mn}} = -1.0 \, \text{V vs. SHE} \]

Solution:

(a) The cathodic reaction is:

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \]

The equilibrium potential for cathodic reaction is calculated using the Nernst equation:

\[ e_{\text{O}_2|\text{OH}^-} = 1.227 - 0.059(\text{pH}) \]

The anodic Tafel equation for iron dissolution is:

\[ \eta_a = b_a \log \left( \frac{i_a}{i_a^0} \right) \]

where

\[ \eta_a = E_{\text{corr}} - e_{\text{eq,Fe}^{+2}|\text{Fe}} \]

\[ \eta_c = b_c \log \left( \frac{i_c}{i_c^0} \right) \]
where

\[ \eta_c = E_{\text{corr}} - \epsilon_{\text{eq,O}_2|\text{OH}^-} \]

The corrosion currents and potentials presented in Fig. 3.18 are obtained by constructing the Evans diagram. The points \( (\epsilon_{\text{eq,Fe}^{3+} | \text{Fe}}, i_{\text{Fe}^{3+} | \text{Fe}}^0) \) and \( (\epsilon_{\text{eq,O}_2|\text{OH}^-}, i_{\text{O}_2|\text{OH}^-}^0) \) are marked on a semilogarithmic graph of \( E \) vs. \( i \). From the points marked, straight lines with the slope \( b_c \) from \( (\epsilon_{\text{eq,O}_2|\text{OH}^-}, i_{\text{O}_2|\text{OH}^-}^0) \) and \( b_a \) from \( (\epsilon_{\text{eq,Fe}^{3+} | \text{Fe}}, i_{\text{Fe}^{3+} | \text{Fe}}^0) \) are extended. The two straight lines intersect at the point \( (E_{\text{corr}}, I_{\text{corr}}) \) giving the corrosion potential and the corrosion current, respectively. The corrosion current and the corrosion potential can also be estimated analytically by simultaneously solving the anodic and cathodic Tafel equations.

As shown in Fig. 3.18, similar cathodic Tafel plots are constructed for each limiting current. The point of intersection of the anodic and cathodic curves provides the corrosion current and corrosion potential as a function of the electrolyte velocity for the oxygen–iron system. Note that the value of the sacrificial current increases with increased electrolyte velocity.

From the plots, it is seen that the corrosion current increases as the angular velocity increases from 0 to 30. However, when the velocity is increased further, the reduction of oxygen becomes activation controlled. As a result, the corrosion rate becomes independent of velocity. Table 3.5 summarizes the corrosion current and the corrosion potential as a function of electrolyte velocity. The data were taken from Fig. 3.18.

(b) To estimate the corrosion current and the corrosion potential when sacrificial Zn-Mn alloy is short circuited with iron, the anodic Tafel line for Zn-Mn sacrificial alloy is plotted in Fig. 3.19. The point of intersection of the Zn-Mn dissolution line and cathodic oxygen Tafel line provides the value of the galvanic current (GC) or impressed current (IC) and the corrosion potential.

The intersection of the anodic Zn-Mn alloy dissolution line and the cathodic oxygen reduction line for different electrolyte velocities gives a new value for \( E_{\text{corr}} \) and
galvanic current provided by Zn-Mn. Figure 3.19 and Table 3.6 indicate that by decreasing the limiting current of oxygen, the cathodic polarization due to the sacrificial anode is increased. Also, the galvanic current needed to protect the system decreases. For each oxygen diffusion limiting current, the corrosion current and the corrosion potential for the iron dissolution system were estimated from Fig. 3.19 and are summarized in Table 3.6 for the for the iron dissolution system.

The results indicate that the system is underprotected when the velocity of the electrolyte is greater than or equal to 40 m/sec, and it is overprotected when the velocity is less than or equal to 30 m/s.

---

**Table 3.5** Estimated Corrosion Current and Corrosion Potential as a Function of Electrolyte Velocity

<table>
<thead>
<tr>
<th>Electrolyte Velocity (m/s)</th>
<th>Corrosion Current (A/cm²)</th>
<th>Corrosion Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.001</td>
<td>−0.260</td>
</tr>
<tr>
<td>10</td>
<td>0.010</td>
<td>−0.160</td>
</tr>
<tr>
<td>20</td>
<td>0.100</td>
<td>−0.060</td>
</tr>
<tr>
<td>30</td>
<td>0.307</td>
<td>−0.012</td>
</tr>
<tr>
<td>40</td>
<td>0.307</td>
<td>−0.120</td>
</tr>
</tbody>
</table>

![Corrosion current as a function of electrolyte velocity](image)

**Table 3.6** Corrosion Current and Corrosion Potential as a Function of Electrolyte Velocity in Zn-Mn Sacrificial Alloy

<table>
<thead>
<tr>
<th>Electrolyte Velocity (m/s)</th>
<th>Corrosion Current (A/cm²)</th>
<th>Corrosion Potential (V vs. SHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$4.05 \times 10^{-8}$</td>
<td>−0.8</td>
</tr>
<tr>
<td>10</td>
<td>$4.05 \times 10^{-7}$</td>
<td>−0.7</td>
</tr>
<tr>
<td>20</td>
<td>$4.05 \times 10^{-6}$</td>
<td>−0.6</td>
</tr>
<tr>
<td>30</td>
<td>$4.05 \times 10^{-6}$</td>
<td>−0.5</td>
</tr>
<tr>
<td>40</td>
<td>$4.05 \times 10^{-5}$</td>
<td>−0.4</td>
</tr>
</tbody>
</table>
EXERCISES

E3.1. The potential of a zinc electrode on which Zn deposits from a 0.1 M ZnSO₄ solution is −1.1 V vs. SCE.
   (a) Determine the zinc deposition potential on the hydrogen scale.
   (b) Determine whether oxidation or reduction occurs at this potential.

E3.2. Copper is immersed in a solution of AgCl where the activity of Ag⁺ is 0.01 M. The following ion exchange reaction occurs during corrosion of copper:

\[
\text{Cu} + 2\text{Ag}^+ \rightarrow \text{Cu}^{2+} + 2\text{Ag}
\]

Estimate the concentration of Cu²⁺ that would trigger the copper corrosion to stop.

E3.3. Calculate the anodic exchange current density for tin for an overpotential of 0.2 V if the corrosion current is 0.5 A/cm². The anodic Tafel slope, \(b_a\), is 0.05 V/decade.

E3.4. Using the Tafel equations, derive:
   (a) The corrosion current equation (dependence of \(I_{corr}\) on \(i_{H_2}\) and \(i_M\)).
   (b) The corrosion potential equation (dependence of \(E_{corr}\) on \(i_{H_2}\) and \(i_M\)).

E3.5. Construct an Evans diagram (\(E\) vs. \(\log i\)) for the corrosion of silver in a hydrogen-saturated 0.1 M HCl solution where the activity of Ag²⁺ is \(10^{-18}\) M. The corrosion reaction data is as follows:

\[
\begin{align*}
[\text{Ag}^{2+}] &= 10^{-18}\text{ M} & [\text{H}^+] &= 0.1\text{ M} \\
\alpha_c &= -0.0824\text{ V vs. SHE} & b_a &= 0.100\text{ V/decade} & b_c &= -0.100\text{ V/decade} \\
\iota_{Ag}^\circ &= 0.8\text{ A/cm}^2 & \iota_{H_2}^\circ &= 0.15\text{ A/cm}^2
\end{align*}
\]

Calculate:
   (a) Equilibrium potentials of the hydrogen and Ag redox reaction.
   (b) Corrosion current and corrosion potential.
   (c) Protection current to prevent corrosion.

E3.6. A lead electrode is immersed in an oxygen-saturated 0.1 M PbSO₄ solution. Calculate and plot the corrosion current at pH between 3 and 6. The Tafel constants are \(b_a = -b_c = 0.10\text{ V/decade}\) and the exchange current densities for lead and oxygen reduction are \(10^{-1}\) and \(10^{-2}\) A/cm², respectively.

E3.7. Iron corrodes in a solution saturated with oxygen. The pH of the solution is 7 and the partial pressure of oxygen is 1 atm.
   (a) Calculate the corrosion current and corrosion potential of the system.
   (b) Calculate the protection current required to reduce the corrosion current to zero.
Additional information:

\[ [\text{Fe}] = 0.7 \text{M} \quad \text{pH} = 7 \quad \text{P}_{\text{O}_2} = 1 \text{ atm} \]

\[ b_a = 0.08 \text{V/decade} \quad b_c = -0.11 \text{V/decade} \]

\[ i_{\text{Fe}}^0 = 10^{-5} \text{A/cm}^2 \quad i_{\text{OH}^-}^0 = 10^{-6} \text{A/cm}^2 \]

**E3.8.** Derive an expression for the slope of the corrosion rate vs. pH for zinc in a 0.01 M ZnCl\(_2\) solution. Assume that all zinc acts as a cathode and assume that there is no concentration polarization.

**E3.9.** The exchange current density and the cathodic Tafel slope, \(b_c\), of platinum in a deaerated H\(_2\)SO\(_4\) solution with a pH of 2.0 are \(7.6 \times 10^{-6}\) and \(-0.025 \text{ V/decade}\), respectively. Calculate the current in A/cm\(^2\) when platinum is polarized cathodically at \(-0.334 \text{ V vs. SCE}\).

**E3.10.** Calculate the limiting current density for oxygen reduction in alkaline solution if the oxygen concentration is 0.4 mol/m\(^3\), the diffusion coefficient, \(D_{\text{O}_2}\), is equal to \(5.0 \times 10^{-10} \text{ m}^2/\text{s}\), and the diffusion layer thickness is 195.3 \(\mu\)m.

**E3.11.** Nickel is deposited at a current density of 75 A/m\(^2\). Calculate the limiting current if the reduction occurs at a concentration overpotential of \(-150 \text{ mV}\).

**E3.12.** Calculate the corrosion potential, corrosion current, and protection current needed to stop corrosion for cadmium in a corrosive deaerated medium.

Additional information:

\[ [\text{Cd}^{2+}] = 10^{-5} \text{M} \quad \text{pH} = 1 \quad a_c = -0.360 \text{V vs. SHE} \]

\[ b_a = 0.100 \text{V/decade} \quad b_c = -0.120 \text{V/decade} \quad i_{\text{Cd}}^0 = 10^{-3} \text{A/cm}^2 \]

**REFERENCES**