Corrosion Kinetics

Course Outline

<table>
<thead>
<tr>
<th>Week</th>
<th>Topic</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Introduction: Reactivity types, corrosion definition, forms, effects, costs, risk management, control measures</td>
</tr>
<tr>
<td>2-3</td>
<td>Corrosion thermodynamics: Corrosion reactions, cell requirements, free energy change, electrochemical potential, Nernst equation, Eh-pH (Pourbaix) diagrams, reference electrodes</td>
</tr>
<tr>
<td>4-6</td>
<td>Corrosion kinetics: Faraday's law, electrical double layer, exchange current density, activation and mass transport control, mixed potential theory, polarization diagrams, passivity</td>
</tr>
<tr>
<td>7</td>
<td>Mid Semester Exams</td>
</tr>
</tbody>
</table>

Why Study Corrosion Kinetics?

- Corrosion is thermodynamically possible for most aqueous environmental conditions
  - Knowledge of corrosion rate is of primary importance
- Corrosion in aqueous systems governed by electrochemical reactions
- Knowledge of electrochemical reaction kinetics is of primary importance
  - Develop more corrosion-resistant alloys
  - Improve corrosion control methods

Electrochemical Reactions

- Anodic reaction produces electrons & cathodic reaction consumes electrons
  - Rate of electron flow to or from a reacting interface is a measure of the reaction rate
  - Electron flow conveniently measured as current (I), in amperes
  - 1-ampere = 1-columb of charge (6.82 x 10^18 electrons/second)

Corrosion involves a loss in mass

Faraday’s Law

\[ m = \frac{Ita}{nF} \]

- \( m \) = mass reacted (g)
- \( I \) = current (A)
- \( a \) = atomic weight (g/mol)
- \( t \) = time (s)
- \( F \) = Faraday’s constant (96,500 C-equiv)
- \( n \) = number of electrons exchange

Faraday’s Law

\[ r = \frac{m}{At} = \frac{Ita}{nF} \frac{1}{At} = \frac{ia}{nF} \]

- \( r \) = rate (g/cm²/s)
- \( A \) = surface area (cm²)
- \( i \) = current density (A/cm²)
**Faraday's Law**

Assume Current Density = 1 µA/cm²

\[ r = \frac{1}{nFD} \]

- Density of zinc = 7.13 g/cm³
- Atomic weight of zinc = 65.38 g/mol
- Number of zinc electrons transferred = 2

\[ r = 4.75 \times 10^{-11} \text{ cm/s} \]
\[ r = 0.59 \text{ mpy (0.015 mm/yr)} \]

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**Equivalent Weight of an Alloy**

\[ EW = \frac{1}{N_{eq}} \text{ where } N_{eq} = \sum \left( \frac{f_i}{a_i/n_i} \right) = \sum \left( \frac{f_i n_i}{a_i} \right) \]

- \( N_{eq} \) = Total number of equivalents;
- \( f_i \) = mass fraction
- \( a_i \) = atomic weight
- \( n_i \) = electron exchanged

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**Consider type 304L stainless steel**

<table>
<thead>
<tr>
<th>Element</th>
<th>wt. %</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>71.75</td>
<td>2</td>
</tr>
<tr>
<td>Cr</td>
<td>19.00</td>
<td>3</td>
</tr>
<tr>
<td>Ni</td>
<td>9.25</td>
<td>2</td>
</tr>
</tbody>
</table>

\[ N_{eq} = \left( \frac{0.7175 \times 2}{55.85} \right) + \left( \frac{0.19 \times 3}{52.00} \right) + \left( \frac{0.0925 \times 2}{58.71} \right) = 0.03981 \]

Equivalent Weight = 25.12

---

**Assume Current Density of 1 µA/cm²**

\[ r = \frac{i(EW)}{FD} \]

- \( r = 3.29 \times 10^{-11} \text{ cm/s} \]
- \( r = 0.41 \text{ mpy (0.010 mm/yr)} \)

Density of Type 304L SS = 7.9 g/cm³

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**Corrosion Rate Conversion**

<table>
<thead>
<tr>
<th>mA cm⁻²</th>
<th>mm y⁻¹</th>
<th>mpy</th>
<th>g m⁻² day⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.28 M/nd</td>
<td>129 M/nd</td>
<td>8.95 M/m</td>
</tr>
<tr>
<td>0.306 nd/M</td>
<td>1</td>
<td>39.4</td>
<td>2.74 d</td>
</tr>
<tr>
<td>0.00777 nd/M</td>
<td>0.0254</td>
<td>1</td>
<td>0.0694 d</td>
</tr>
<tr>
<td>0.112 n/M</td>
<td>0.365 /d</td>
<td>14.4 /d</td>
<td>1</td>
</tr>
</tbody>
</table>

where

- \( \text{mA cm}^2 \) = milliampere per cm²
- \( \text{mm y}^{-1} \) = millimeter per year
- \( \text{mpy} \) = millipond per year
- \( g \text{ m}^{-2} \text{ day}^{-1} \) = grams per square meter per day

\*Note: the table should be read from left to right, i.e., 1 mA cm⁻² = (3.28 M/nd) mm y⁻¹ = (129 M/nd) mpy = (8.95 M/m) g m⁻² day⁻¹

**Exchange Current Density**

\[ 2H^+ + 2e^- = H_2 (g) \]

Forward Reaction

\[ r_f = \frac{i_f a}{nF} \]

Reverse Reaction

\[ i_r = \frac{i_f a}{nF} \]

where

- \( r_f \) = Forward Reaction current density
- \( i_f \) = Forward Reaction current
- \( a \) = Active area
- \( n \) = Number of electrons
- \( F \) = Faraday's constant

Note: the table should be read from left to right, i.e., 1 mA cm⁻² = (3.28 M/nd) mm y⁻¹ = (129 M/nd) mpy = (8.95 M/m) g m⁻² day⁻¹
**Exchange Current Density**

<table>
<thead>
<tr>
<th>Metal</th>
<th>$i_0$ (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb, Hg</td>
<td>$10^{16}$</td>
</tr>
<tr>
<td>Zn</td>
<td>$10^{11}$</td>
</tr>
<tr>
<td>Sn, Al</td>
<td>$10^{10}$</td>
</tr>
<tr>
<td>Ni, Ag, Cu</td>
<td>$10^8$</td>
</tr>
<tr>
<td>Fe, Au</td>
<td>$10^7$</td>
</tr>
<tr>
<td>Pd, Rh</td>
<td>$10^4$</td>
</tr>
<tr>
<td>Pt</td>
<td>$10^3$</td>
</tr>
</tbody>
</table>

Approximate exchange current densities for hydrogen reduction on various metals.

**Polarisation**

Polarization is a change in potential caused by the passage of a current

Overpotential is the potential difference between two half cell reactions

Equilibrium potential for cathodic reaction = $E_{oc}$
Equilibrium potential for anodic reaction = $E_{oa}$
Real potential = $E$

Cathodic Overpotential $\eta_c = E - E_{oc} < 0$
Anodic Overpotential $\eta_a = E - E_{oa} > 0$

**The Polarized Cell**

**Types of Polarisation**

1. Activation overpotential (charge transfer)
2. Concentration overpotential (mass transport)
3. Resistance polarisation (Ohmic drop)

**Activation Polarisation**

- Caused by slow electrode reaction => reaction requires activation energy to proceed.
- The rate of a reaction is determined by the slowest step - rate determining step.
- Hydrogen evolution at a platinum electrode:
  - $H^+ + e^- \rightarrow H_{ads}$
  - $2H_{ads} \rightarrow H_2$
**Concentration Polarisation**

- Transport of reactants is the rate determining step.
- Take cathodic reduction of H⁺ as an example:
  
  \[ 2H^+ + 2e = H_2 \]

- At high reaction rates, cathodic reactions deplete the adjacent solution of the dissolved species.

**Concentration Polarisation**

- Fick’s Law: 
  
  \[ \frac{dn}{dt} = -D \frac{dc}{dx} \times 10^{-3} \]  

  where \( \frac{dn}{dt} \) is the mass transport in x direction in mol/cm²s, \( D \) is the diffusion coefficient in cm²/s, and \( c \) is the concentration in mol/liter

- Faraday’s law:
  
  \[ r = \frac{m}{Av} = \frac{I}{AnF} = \frac{i}{nF} \]  

- Under steady state, 
  
  mass transfer rate = reaction rate
  
  \[ i = DnF \frac{C_k - C_0}{\delta} \times 10^{-3} \]

**Concentration Polarisation**

- Maximum transport and reaction rate are attained when \( C_0 \) approaches zero and the current density approaches the **limiting current density**:
  
  \[ i_t = DnF \frac{C_k \times 10^{-3}}{\delta} \]

  where \( D_z \) is the diffusivity of the reacting species \( Z \) (H⁺ in this example)

- \( i_t \) will be increased if:
  
  - \( C_0 \), bulk concentration increases
  - \( T \), temperature increases which increases \( D_z \)
  - \( \delta \), decreases due to higher velocity/flow/solution agitation

**Concentration Polarisation**

- Process controlled by diffusion in electrolyte

**Concentration Polarisation**

- Double layer at electrode-solution interface

**Double Layer**

- Potential distribution across distance

**Concentration Polarisation**

- Concentration profile of H⁺ in solution near the surface of an electrode (cathode)
IR Drop

- The drop in potential between the electrode and the tip of Luggin probe equals iR.
- If \( l \) is the length of the electrode path of cross sectional area, \( k \) is the specific conductivity, and \( i \) is the current density then resistance
  \[
  R = \frac{l}{k}
  \]
- iR drop (V) = \( \frac{il}{k} \)

Combined Polarisation

- Total polarization of an electrode is the sum of the individual contributions,
  \[
  \eta_T = \eta_a + \eta_c + \eta_k
  \]
- If neglect IR drop or resistance polarization is neglected then:
  \[
  \eta_T = \eta_a + \eta_c
  \]

Effect of Potential on Reaction Rate
- Anodic & Cathodic

Butler-Vomer Equation

The expression relating the overpotential, \( \eta \), to the net current, \( i \), is the Butler-Vomer equation:

\[
  i = i_o \left[ \exp \left( \frac{\beta nF}{RT} \eta \right) - \exp \left( -1 - \frac{\beta nF}{RT} \eta \right) \right]
\]

where:
- \( R \) = gas constant;
- \( T \) = absolute temperature;
- \( n \) = no. charges transferred (= valency);
- \( F \) = Faraday (96,500 coul/mol);
- \( \beta \) = “symmetry coefficient” (\( \rightarrow 0.5 \));
- \( i_o \) = exchange current density (a constant for the system).

The first term in \( \{ \} \) in B-V describes the forward (metal dissolution, anodic) reaction; the second term in \( \{ \} \) describes the backward (metal deposition, cathodic) reaction.

Tafel Behaviour (Activation Control)

Thus, for metal dissolution:

\[
  i_a = i_o \exp \left( \frac{\beta nF}{RT} \eta_a \right)
\]

where …

\[
  \eta_a = b_a \log \frac{i}{i_o}
\]

Tafel coefficient: \( b_a = \frac{2.303RT}{\beta nF} \)

For metal deposition:

\[
  b_c = \frac{2.303RT}{\beta nF}
\]

\[
  i_a = i_o 10^{\left(\frac{E-E_1}{b_a}\right)}
\]
Tafel Behaviour (Activation Control)

- Cathodic Polarization
\[ \eta_c = \beta_c \log \left( \frac{i_c}{i_0} \right) \]
- Anodic Polarization
\[ \eta_a = \beta_a \log \left( \frac{i_a}{i_0} \right) \]

\[ \eta = \text{Overpotential}; \quad \beta = \text{Tafel Constant} \]
\[ \beta_c = \text{Positive}; \quad \beta_a = \text{Negative} \]
\[ +0.1 \text{ V/decade} \]

Combining these equations, we get:

Evans Diagram

\[ \Pi_{\text{Total}} = \Pi_{\text{Act}} - \Pi_{\text{Diff}} \]
\[ \Pi_{\text{Total}} = \beta \log \frac{i}{i_0} - 2.3 \frac{\beta}{\beta_c \eta} \log \left[ 1 - \frac{i}{i_0} \right] \]

Effect of Potential on Reaction Rate
- Diffusion controlled
\[ i = i_L \]

Effect of Potential on Reaction Rate
- Passivity
\[ i = i_{\text{pass}} \]

Combined Polarization

Polarisation Diagram of SS in aerated dilute H\textsubscript{2}SO\textsubscript{4}

1. Active loop
2. Passive loop
3. Activation-controlled region of oxygen reduction rxn
4. Diffusion-controlled region of oxygen reduction rxn
5. Hydrogen evolution (activation controlled)
Mixed Potentials – Concepts and Basics

- Total rate of oxidation must be equal to total rate of reduction.
  - Sum of anodic oxidation currents must be equal to sum of cathodic reduction currents.

- General anodic reaction: \( M = M^{2+} + 2e \)

- Cathodic reactions can be different depending on environmental conditions.

Mixed Potentials – Concepts and Basics

- Evolution of hydrogen from acid or neutral solution:
  - \( 2H^+ + 2e = H_2 \) (acid)
  - \( 2H_2O + 2e = H_2 + 2OH^- \) (neutral or alkaline)

- Reduction of dissolved oxygen in acid or neutral solution:
  - \( O_2 + 4H^+ + 4e = 2H_2O \) (acid)
  - \( O_2 + 2H_2O + 4e = 4OH^- \) (neutral)

- Reduction of dissolved oxidizers such as ferric ions:
  - \( Fe^{3+} + e = Fe^{2+} \)

At \( E_{corr} \) rates of anodic and cathodic reactions are equal.

\[ i_a = i_c = i_{corr}, \text{ at } E_{corr} \]
The anodic line of Evans diagram merges with experimental anodic polarization curve.

The cathodic line of Evans diagram merges with experimental cathodic polarization curve.

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

$Fe \rightarrow Fe^{2+} + 2e^-$

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