COMPUTATION OF CORROSION

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1 INTRODUCTION

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1.1 ECONOMIC SIGNIFICANCE

• CONSEQUENCES OF CORROSION
  – WASTE OF UP TO ~3% OF GNP
  – WASTE OF NATURAL RESOURCES
  – ECOLOGICAL DAMAGE

• UP TO ~1% OF THE WASTED GNP COULD BE SAVED IF EXISTING KNOWLEDGE IS APPLIED!
1.2 DEFINITION OF CORROSION

• ELECTROCHEMICAL WEAR OF METALS EXPOSED TO REACTIVE AQUEOUS ENVIRONMENTS

• WEAR PRODUCTS ARE STABLE METAL COMPOUNDS

• THERE ARE MANY DIFFERENT FORMS OF CORROSION
1.3 THERMODYNAMICS

- System; Surroundings
- Equilibrium
- Standard State
- Laws of Thermodynamics
- Chemical Potential
- Equilibrium Constant
- Reaction Isotherm
1.4 ELECTROCHEMISTRY

- ELECTROCHEMICAL POTENTIAL
- ELECTROCHEMICAL CELLS
  - OXIDATION REACTION (ANODE)
  - REDUCTION REACTION (CATHODE)
- HALF CELL AND SINGLE POTENTIAL
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- CHEMICAL REACTION RATE
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2 CORROSION THERMODYNAMICS

2.1 CHEMICAL SYSTEMS

2.2 ELECTROCHEMICAL SYSTEMS

2.3 DIAGRAMS POTENTIAL-pH

2.4 IMMUNITY, PASSIVITY AND CORROSION

2.5 EXAMPLES
2.1 CHEMICAL SYSTEMS I

• GIBBS FREE ENERGY
  \[ G = H - TS \]

• EQUILIBRIUM CRITERION
  \[ \Delta G = 0 \]

• CHEMICAL POTENTIAL
  \[ \mu_i = \frac{\delta G}{\delta n_i} = \mu_i^0 + RT \ln a_i \]
2.1 CHEMICAL SYSTEMS II

- GENERIC CHEMICAL REACTION
  \[ \sum \nu_i M_i = 0 \]

- CRITERION FOR REACTION EQUILIBRIUM
  \[ \sum \nu_i \mu_i^0 + RT \sum \nu_i \ln a_i = 0 \]

- IN TERMS OF EQUILIBRIUM CONSTANT
  \[ -\sum \nu_i \mu_i^0 = RT \sum \nu_i \ln a_i = RT \ln K \]
2.1 CHEMICAL SYSTEMS III

• EXAMPLES
  – DISSOCIATION OF WATER
    \[ H_2O = H^+ + OH^- \]
    \[ K = a_{H^+} a_{OH^-}/a_{H_2O} = a_{H^+} a_{OH^-} = 10^{-14} \]
  – PRECIPITATION OF METAL HYDROXIDE
    \[ K = (a_{H^+})^2/ a_{Mg^{2+}} = 10^{-16.95} \]
2.2 ELECTROCHEMICAL SYSTEMS I

• GENERIC ELECTROCHEMICAL REACTION

\[ \sum \nu_i M_i + ne = 0 \]

• CRITERION FOR ELECTROCHEMICAL EQUILIBRIUM

\[ \sum \nu_i \mu_i^0 + RT \sum \nu_i \ln a_i - 23061 n E_o = 0 \]

• WHERE \( E_o \) IS THE EQUILIBRIUM POTENTIAL
2.2 ELECTROCHEMICAL SYSTEMS II

- IN TERMS OF THE EQUILIBRIUM POTENTIAL (NERNST EQUATION)
  \[ E_0 = E^{\circ} + \frac{(2.3RT/nF)\sum \nu_i \log a_i}{23061\ n} \]

- WHERE
  \[ E^{\circ} = \frac{\sum \nu_i \mu_i^{\circ}}{23061\ n} \]

- IS THE STANDARD EQUILIBRIUM POTENTIAL
2.2 ELECTROCHEMICAL SYSTEMS III

- **EXAMPLE: THE STANDARD HYDROGEN ELECTRODE**
  
  \[ 2 \text{H}^+ + 2 \text{e}^- = \text{H}_2 \]

- **DATA**
  
  \[ \mu_{\text{H}^+}^0 = \mu_{\text{H}_2}^0 = 0 \text{ cal/mol} \]

- **THUS**
  
  \[ E^0_o = \sum v_i \mu_i^o / (23061 \text{ n}) = 0 \]
2.2 ELECTROCHEMICAL SYSTEMS IV

- **THUS**
  
  \[ E_0 = E_0^\circ + (2.3RT/nF) \sum \nu_i \log a_i \]

  \[ = 0.0 + 0.059 \log a_{H^+} - 0.0295 \log P_{H_2} \]

- **AND FOR** \( P_{H_2} = 1 \text{ atm} \)
  
  \[ E_0 = 0.0 - 0.059 \text{ pH} \]
2.2 ELECTROCHEMICAL SYSTEMS V

• POSSIBILITY OF ELECTROCHEMICAL REACTIONS
  – IF $E = E_0$ >> EQUILIBRIUM (NO REACTION)
  – IF $E > E_0$ >> OXIDATION POSSIBLE
  – IF $E < E_0$ >> REDUCTION POSSIBLE
2.2 ELECTROCHEMICAL SYSTEMS VI

• THE VELOCITY OF A REACTION (AS MEASURED BY THE INTENSITY OF THE REACTION CURRENT \( i \)) IS EITHER ZERO OR OF THE SAME SIGN AS ITS OVERPOTENTIAL

\[
(E - E_0) i = 0 \quad \text{or} \quad (E - E_0) i > 0
\]
2.3 DIAGRAMS E-pH I

- FIRST PRESENTED BY POURBAIX
- GRAPHICAL REPRESENTATIONS OF E₀-pH RELATIONSHIPS FOR SELECTED REDOX COUPLES
- OBTAINED FROM NERNST EQUATIONS
- USED TO IDENTIFY REGIONS OF PREDOMINANCE
2.3 DIAGRAMS E-pH II

• HYDROGEN EVOLUTION (LINE a)
  
  \[ 2 \text{H}^+ + 2 \text{e} = \text{H}_2 \]
  
  \[ E = 0.0 - 0.059 \text{pH} \]

• OXYGEN REDUCTION (LINE b)
  
  \[ \text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e} = 4 \text{OH}^- \]
  
  \[ E = 1.228 - 0.059 \text{pH} \]
2.3 DIAGRAMS E-pH III

• MAIN REACTION TYPES
  – REACTIONS DEPENDING ON pH ONLY
    \[ \text{Fe}^{3+} + \text{H}_2\text{O} = \text{Fe(OH)}^2+ + \text{H}^+ \]
  – REACTIONS DEPENDING ON E ONLY
    \[ \text{Fe} = \text{Fe}^{2+} + 2\text{e} \]
  – REACTIONS DEPENDING ON pH AND E
    \[ \text{Fe}^{3+} + \text{H}_2\text{O} = \text{Fe(OH)}^2+ + \text{H}^+ + \text{e} \]
  – REACTIONS INDEPENDENT OF pH AND E
    \[ \text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3 \]
2.3 DIAGRAMS E-pH IV

- DIAGRAM CONSTRUCTION PROCEDURE
  - DETERMINE SPECIES INVOLVED
  - WRITE DOWN REACTIONS FOR ALL SPECIES INVOLVED
  - WRITE DOWN NERNST EQUATIONS FOR ALL REACTIONS USING $a_i = 10^{-6}$
  - FIND E AND pH VALUES FOR INTERSECTIONS BETWEEN REACTIONS
2.4 IMMUNITY, PASSIVITY AND CORROSION

- **IMMUNITY**: DOMAIN IN E-pH SPACE WHERE THE METAL PHASE IS THERMODYNAMICALLY STABLE

- **PASSIVITY**: DOMAIN IN E-pH SPACE WHERE AN INSOLUBLE FILM IS THERMODYNAMICALLY STABLE

- **CORROSION**: DOMAIN IN E-pH SPACE WHERE SOLUBLE PRODUCTS ARE THERMODYNAMICALLY STABLE
2.5 EXAMPLES I

Fe/Fe2+/Fe3+/Fe3O4/Fe2O3 SYSTEM

• REACTIONS (NUMBERS FROM ATLAS)

   Fe$^{2+}$ = Fe$^{3+}$ + 1e ..........(4)
   3Fe + 4H$_2$O = Fe$_3$O$_4$ + 8H$^+$ + 8e ......(13)
   2Fe$_3$O$_4$ + H$_2$O = 3Fe$_2$O$_3$ + 2H$^+$ + 2e ...(17)
   2Fe$^{3+}$ + 3H$_2$O = Fe$_2$O$_3$ + 6H$^+$ .....(20)
   Fe = Fe$^{2+}$ + 2e ..............(23)
   3Fe$^{2+}$ + 4H$_2$O = Fe$_3$O$_4$ + 8H$^+$ + 2e ...(26)
   2Fe$^{2+}$ + 3H$_2$O = Fe$_2$O$_3$ + 6H$^+$ + 2e ...(28)
2.5 EXAMPLES II
Fe/Fe$_2$+/Fe$_3$+/Fe$_3$O$_4$/Fe$_2$O$_3$ SYSTEM

• EQUILIBRIUM POTENTIALS/EQNS

$E_4 = 0.771 + 0.0591 \log(\text{Fe}_3^+/$Fe$_2^+$)

$E_{13} = -0.085 - 0.0591 \ \text{pH}$

$E_{17} = 0.221 - 0.0591 \ \text{pH}$

$\log(\text{Fe}_3^+)_{20} = -0.72 - 3 \ \text{pH}$

$E_{23} = -0.44 + 0.0295 \log(\text{Fe}_2^+)$

$E_{26} = 0.98 - 0.2364 \ \text{pH} - 0.0886 \log(\text{Fe}_2^+)$

$E_{28} = 0.728 - 0.1773 \ \text{pH} - 0.0591 \log(\text{Fe}_2^+)$
2.5 EXAMPLES III

Fe/Fe2+/Fe3+/Fe3O4/Fe2O3 SYSTEM

• INTERSECTION 1: 20-28
• INTERSECTION 2: 17-26-28
• INTERSECTION 3: 13-23-26
• VERTICAL LINES: 20
• HORIZONTAL LINES: 23
2.5 EXAMPLES IV

• EXERCISE: CONSTRUCT POURBAIX DIAGRAMS
  – Mg/Mg²⁺/Mg(OH)₂ SYSTEM
    \[ \text{Mg}^{2+} + 2e^- = \text{Mg} \]
    \[ E_3 = -2.363 + 0.0295 \log(\text{Mg}^{2+}) \]
  – OTHER SYSTEM OF YOUR CHOICE
3 ELECTRODE KINETICS

3.1 MECHANISMS OF ELECTRODE REACTIONS

3.2 EXCHANGE CURRENT

3.3 POLARIZATION AND OVERVOLTAGE

3.4 TYPES OF OVERVOLTAGE

3.5 EXAMPLES
3.1 MECHANISMS OF ELECTRODE REACTIONS I

- ELECTRODE PROCESSES ARE HETEROGENEOUS REACTIONS
- THE ELECTRODE-ELECTROLYTE INTERFACE HAS COMPLEX STRUCTURE (ELECTROCHEMICAL DOUBLE LAYER/DIFFUSE LAYER)
- THE STRUCTURE OF THE ECDL INFLUENCES REACTION RATES
3.1 MECHANISMS OF ELECTRODE REACTIONS II

1.- MASS TRANSFER OF REACTANTS FROM BULK OF SOLUTION TO ELECTRODE BOUNDARY LAYER

2.- ADSORPTION OF REACTANTS ONTO ELECTROCHEMICAL DOUBLE LAYER

3.- DEHYDRATION/DESOLVATION
3.1 MECHANISMS OF ELECTRODE REACTIONS III

4.- CHEMICAL CHANGES LEADING TO INTERMEDIARIES

5.- ELECTRON TRANSFER

6.- ADSORPTION OF REACTION PRODUCTS

7.- DESORPTION OF REACTION PRODUCTS
3.1 MECHANISMS OF ELECTRODE REACTIONS IV

8.- SECONDARY CONVERSION OF PRIMARY PRODUCTS

9.- MASS TRANSFER OF PRODUCTS FROM BOUNDARY LAYER INTO BULK OF THE SOLUTION
3.1 MECHANISMS OF ELECTRODE REACTIONS V

THE MOST CHARACTERISTIC FEATURE OF ELECTRODE PROCESSES IS THE DEPENDENCE OF THE ACTIVATION ENERGY FOR THE ELECTRON TRANSFER STEP ON THE POTENTIAL DIFFERENCE BETWEEN ELECTRODE AND SOLUTION.
3.2 EXCHANGE CURRENT I

THE CURRENT DENSITY $i$ (A/m$^2$) IS A MEASURE OF THE RATE OF ELECTROCHEMICAL REACTION

$$i = z F v$$

$z = \text{number of electrons/molecule}$

$F = \text{Faraday’s constant} = 96487 \text{ Coulomb/mol}$

$v = \text{reaction rate} \ (\text{mole/m}^2 \text{ s})$
3.2 EXCHANGE CURRENT II

- THE EQUILIBRIUM AT A REVERSIBLE ELECTRODE IS DYNAMIC

\[ v_a = v_c \]
\[ i_a = i_c \]

- WHERE

\( v_a \) = RATE OF ANODIC (OXIDATION) PROCESS
\( v_c \) = RATE OF CATHODIC (OXIDATION) PROCESS
3.2 EXCHANGE CURRENT III

EQUILIBRIUM SINGLE ELECTRODE

\[ M = M^{+z} + ze \]
\[ i_a = zF k_a \exp(\alpha_a zF \phi_o/RT) \]
\[ i_c = zF k_c a_{M^{z+}} \exp(-\alpha_c zF \phi_o/RT) \]
\[ i_{net} = i_a + i_c = 0 \]
\[ i_o = i_a = -i_c \]
3.2 EXCHANGE CURRENT IV

$k_a, k_c$ = RATE CONSTANTS FOR ANODIC AND CATHODIC PROCESSES

$\alpha_a, \alpha_c$ = TRANSFER COEFFICIENTS FOR ANODIC AND CATHODIC PROCESSES

$\phi_o$ = (EQUILIBRIUM) ELECTRODE POTENTIAL

$i_o$ = EXCHANGE CURRENT
3.2 EXCHANGE CURRENT V

- FROM THE CONDITION \( i_{\text{net}} = 0 \)
  \[ \phi_o = \frac{RT}{zF(\alpha_a + \alpha_c)} \ln \left[ \frac{k_c a_M^{z+}}{k_a} \right] \]

- FROM THE CONDITION \( i_o = i_a = -i_c \)
  \[ i_o = zF k_a \left[ \frac{k_c a_M^{z+}}{k_a} \right] (\alpha a / (\alpha a + \alpha c)) \]
3.2 EXCHANGE CURRENT VI

- EXAMPLES

\[
\begin{align*}
\text{Ag} & = \text{Ag}^+ + e ; \quad i_o = 10^4 \text{ A/m}^2 \\
\text{Cu} & = \text{Cu}^{2+} + 2e ; \quad i_o = 5 \text{ A/m}^2 \\
\text{Zn} & = \text{Zn}^{2+} + 2e ; \quad i_o = 10^{-2} \text{ A/m}^2 \\
\text{H}_2 & = 2\text{H}^+ + 2e \quad \text{(on Pt)} ; \quad i_o = 10^2 \text{ A/m}^2 \\
\text{H}_2 & = 2\text{H}^+ + 2e \quad \text{(on Fe)} ; \quad i_o = 10^{-2} \text{ A/m}^2 \\
\text{H}_2 & = 2\text{H}^+ + 2e \quad \text{(on Pb)} ; \quad i_o = 10^{-9} \text{ A/m}^2
\end{align*}
\]
3.3 POLARIZATION AND OVERVOLTAGE I

IN A NON-EQUILIBRIUM EQUILIBRIUM ELECTRODE $\phi$ IS DISTINCT FROM $\phi_o$

$$i_a = z F k_a \exp(\alpha_a z F \phi/RT)$$
$$= i_o \exp(\alpha_a z F [\phi - \phi_o]/RT)$$

$$i_c = z F k_c a_{Mz^+} \exp(-\alpha_c z F \phi/RT)$$
$$= i_o \exp(-\alpha_c z F [\phi - \phi_o]/RT)$$
3.3 POLARIZATION AND OVERVOLTAGE II

In a non-equilibrium equilibrium electrode there is a net flow of current, the potential is \( \phi \) and
\[
\eta = \phi - \phi_o \quad \text{(activation overvoltage)}
\]

Overvoltage
\[
i_{\text{net}} = i_o \left\{ \exp(\alpha_a z F \eta/RT) - \exp(-\alpha_c z F \eta/RT) \right\}
\]

Butler-Volmer equation
3.3 POLARIZATION AND OVERVOLTAGE III

• “SMALL” $\eta$ APPROXIMATION

IF $|\eta| < 0.01$ V SINCE $e^x \sim 1 + x$

$$i_{net} = i_o (z F \eta/RT)$$

THE LINEAR “LAW”
3.3 POLARIZATION AND OVERVOLTAGE IV

• “LARGE” $\eta$ APPROXIMATION

(ANODIC POLARIZATION)

IF $\eta > 0.1 \text{ V}$ THEN $i_{\text{net}} \sim i_a$

$i_{\text{net}} = i_o \exp(\alpha_a z F \eta/RT)$ OR

$\eta = b_a \log(i_{\text{net}} / i_o)$

ANODIC TAFEL EQUATION
3.3 POLARIZATION AND OVERVOLTAGE V

- “LARGE” $\eta$ APPROXIMATION

(CATHODIC POLARIZATION)

IF $\eta < -0.1$ V THEN $i_{net} \sim i_c$

$i_{net} = i_o \exp(-\alpha_c z F \eta/RT)$ OR

$\eta = b_c \log(i_{net}/i_o)$

CATHODIC TAFEL EQUATION
3.3 POLARIZATION AND OVERVOLTAGE VI

• EXAMPLES

\[
\begin{align*}
\text{Ag} &= \text{Ag}^+ + e \quad ; \quad b_a = 0.12 \text{ V/decade} \\
\text{Cu} &= \text{Cu}^{2+} + 2e \quad ; \quad b_a = 0.06 \text{ V/decade} \\
\text{Zn} &= \text{Zn}^{2+} + 2e \quad ; \quad b_a = 0.06 \text{ V/decade} \\
\text{H}_2 &= 2\text{H}^+ + 2e \quad (\text{on Pt}) \quad ; \quad b_c = -0.12 \text{ V/decade} \\
\text{H}_2 &= 2\text{H}^+ + 2e \quad (\text{on Fe}) \quad ; \quad b_c = -0.12 \text{ V/decade} \\
\text{H}_2 &= 2\text{H}^+ + 2e \quad (\text{on Pb}) \quad ; \quad b_c = -0.12 \text{ V/decade}
\end{align*}
\]
3.4 TYPES OF OVERVOLTAGE I

- ACTIVATION OVERVOLTAGE
- CONCENTRATION OVERVOLTAGE
- RESISTANCE OVERVOLTAGE
- REACTION OVERVOLTAGE
- NUCLEATION OVERVOLTAGE
3.4 TYPES OF OVERVOLTAGE II

- WHEN THE ELECTRON TRANSFER PROCESS IS FAST, IONIC CONCENTRATION GRADIENTS AT THE ELECTRODE SURFACE GIVE RISE TO CONCENTRATION OVERVOLTAGE

\[ \eta_{\text{conc}} = \frac{RT}{zF} \ln \left( \frac{C_{\text{surf}}}{C_{\text{bulk}}} \right) \]
3.4 TYPES OF OVERVOLTAGE III

- **IONIC CONCENTRATION GRADIENTS PRODUCES CURRENT**

\[
i = - z F D \left( \frac{\delta C}{\delta x} \right) = - z F D \left( C_{surf} - C_{bulk} \right) / \delta
\]

- **D** = DIFFUSION COEFFICIENT (m²/s)
- **δ** = CONCENTRATION BOUNDARY LAYER THICKNESS (m)
3.4 TYPES OF OVERVOLTAGE IV

- IN THE LIMIT WHEN $C_{\text{surf}} \sim 0$, THIS BECOMES THE LIMITING CURRENT DENSITY $i_L$

$$i_L = z F D C_{\text{bulk}} / \delta$$

THUS

$$i/i_L = 1 - C_{\text{surf}} / C_{\text{bulk}}$$

AND

$$\eta_{\text{conc}} = (RT/zF) \ln(1 - i/i_L)$$
3.4 TYPES OF OVERVOLTAGE V

- THE BOUNDARY LAYER THICKNESS DEPENDS ON FLUID FLOW
- IN A ROTATING DISK ELECTRODE (RDE) SYSTEM, LEVICH FOUND
  \[ \delta = 1.61 \, D^{1/3} \, \nu^{1/6} \, \omega^{-1/2} \]

\( \nu = \text{KINEMATIC VISCOSITY (m}^2/\text{s}) \)
\( \omega = \text{DISK ROTATION RATE (rad/s)} \)
3.4 TYPES OF OVERVOLTAGE VI

- IF THE ELECTRICAL RESISTANCE ($R$) TO THE FLOW OF CURRENT ($I$) IN THE ELECTROLYTE BETWEEN ANODE AND CATHODE IS SIGNIFICANT THERE CAN BE (ELECTROLYTE) RESISTANCE OVERVOLTAGE

$$\eta_{\text{res}} = I \cdot R$$
3.5 EXAMPLES I

• EXERCISE: SHOW THAT A NET CURRENT DENSITY OF 1 A/m² IS APPROXIMATELY EQUIVALENT TO A UNIFORM CORROSION WASTAGE RATE OF 1 mm/year
3.5 EXAMPLES II

Fe = Fe^{2+} + 2e

\[ M^{z+} = a_{Fe}^{2+} = 10^{-6} \]

\[ \alpha_a = \alpha_c = 0.5 \]

\[ k_a = 14.9; k_a^b = 1.8 \times 10^{-14} \]  

\[ \phi_o = -0.617 \text{ V} \]

\[ i_o = 10^{-4} \text{ A/m}^2 \]
3.5 EXAMPLES III

• EXERCISE: VERIFY THE GIVEN EXPRESSIONS FOR $\phi_o$ AND $i_o$

• EXERCISE: FIND THE VALUES OF $k_a$ AND $k_c$ FOR THE $\text{Mg} = \text{Mg}^{2+} + 2e$ SYSTEM

• EXERCISE: FIND THE VALUES OF $k_a$ AND $k_c$ FOR OTHER SYSTEM OF YOUR CHOICE
3.5 EXAMPLES IV

• Fe ELECTRODE

\[ i_{\text{net}} = i_o \left\{ e^{38.94\eta} - e^{-38.94\eta} \right\} \]

\begin{tabular}{c c c c c}
\( \eta \ (V) \) & 0.01 & 0.02 & 0.05 & 0.1 \\
\( e^{38.94\eta} \) & 1.47 & 2.18 & 7.00 & 49.11 \\
\( e^{-38.94\eta} \) & 0.68 & 0.46 & 0.14 & 0.02 \\
\( i_{\text{net}} / i_o \) & 0.80 & 1.72 & 6.85 & 49.09 \\
\end{tabular}
3.5 EXAMPLES V

- EXERCISES
  - VERIFY THE GIVEN EXPRESSIONS FOR \( i_a \), \( i_c \) AND \( i_{\text{net}} \) FOR NON-EQUILIBRIUM ELECTRODES
  - EXPLORE THE SENSITIVITY OF \( i_{\text{net}} \) TO THE VALUES OF THE TRANSFER COEFFICIENTS.
  - CALCULATE THE THEORETICAL VALUES OF THE TAFEL SLOPES
3.5 EXAMPLES VI

• EXERCISE: CALCULATE THE LIMITING CURRENT DENSITY FOR THE OXYGEN REDUCTION REACTION IN WATER SATURATED WITH OXYGEN

\[ D \sim 10^{-9} \text{ m}^2/\text{s} \]

\[ C_{\text{bulk}} \sim 0.3 \text{ mole/m}^3 \]
4 CORROSION KINETICS

4.1 ANODIC AND CATHODIC REACTIONS

4.2 POLARIZATION

4.3 WAGNER AND TRAUD’S SUPERPOSITION PRINCIPLE

4.4 STERN AND GEARY’S ANALYSIS

4.5 EXAMPLES
4.1 ANODIC AND CATHODIC REACTIONS I

WHEN A METAL CORRODES IN AN AQUEOUS SOLUTION ANODIC AND CATHODIC SITES DEVELOP ON ITS SURFACE

– SITES MAY BE PERMANENTLY SEPARATED FROM EACH OTHER
– SITES MAY SHIFT CONTINUALLY
4.1 ANODIC AND CATHODIC REACTIONS II

• AT ANODIC SITES OXIDATION OCCURS (i_a)

• AT CATHODIC SITES REDUCTION OCCURS (i_c)

• ALL THE ELECTRONS PRODUCED BY THE ANODIC REACTION ARE CONSUMED BY THE CATHODIC PROCESS
4.1 ANODIC AND CATHODIC REACTIONS III

• SIMPLEST ANODIC REACTION (SINGLE STEP)

\[ M = M^{z+} + ze \]

• EVEN IN THIS CASE A COMPLEX MECHANISM MAY BE INVOLVED
4.1 ANODIC AND CATHODIC REACTIONS IV

- COMPLEX ANODIC REACTION (MULTIPLE STEP)

STEP 1

\[ M + nH_2O = [M(H_2O)_n]^{z_1} + z_1e \]
4.1 ANODIC AND CATHODIC REACTIONS V

- **STEP 2a: INHIBITION**
  \[ M + nH_2O = [M(H_2O)_n]^{z_1} + z_1e \]

- **STEP 2b: COMPLEX IONISATION**
  \[ [M(H_2O)_n]^{z_1} = M^{z^+} + nH_2O + (z-z_1)e \]

- **STEP 2c: PASSIVATION**
  \[ M + (z/2)H_2O = MO_{z/2} + zH^+ + ze \]
4.1 ANODIC AND CATHODIC REACTIONS VI

• COMMON CATHODIC REACTIONS IN CORROSION
  – HYDROGEN EVOLUTION
    \[ 2 \, H^+ + 2e = H_2 \]
  – OXYGEN REDUCTION
    \[ O_2 + 4e + 2H_2O = 4OH^- \]
4.1 ANODIC AND CATHODIC REACTIONS VII

• FOR NON-UNIFORM CORROSION IS BETTER TO USE THE TOTAL CURRENTS (I) RATHER THAN THE CURRENT DENSITIES (i)

• PLOTS OF E vs I_a AND I_c ARE CALLED EVANS DIAGRAMS
4.2 POLARIZATION I

• WHEN A METAL CORRODES ITS ELECTRODE POTENTIAL BECOMES ANODICALLY POLARIZED
  \[ \eta_A > 0 \]

• THE ELECTRODE POTENTIAL OF THE CORRESPONDING CATHODIC REACTION BECOMES CATHODICALLY POLARIZED
  \[ \eta_C < 0 \]
4.2 POLARIZATION II

• BECAUSE OF POLARIZATION THE ELECTRODE POTENTIALS OF THE TWO REACTIONS MOVE TOWARDS EACH OTHER AND IF THE ELECTROLYTE RESISTANCE IS LOW

\[ \phi_a = E_a = \phi_c = E_c = \phi^* = E_{corr} \]

\[ i_a = i_c = i_{corr} \]

\[ I_a = I_c = I_{corr} \]
A FREQUENTLY USED ASSUMPTION IS THAT THE ANODIC AND CATHODIC OVERVOLTAGES ARE ADDITIVE. THIS IS THAT THE ANODIC AND CATHODIC OVERVOLTAGES ARE ADDITIVE.

$$\eta_T = \eta + \eta_{\text{con}} + \eta_{\text{res}} + \eta_{\text{other}}$$
4.2 POLARIZATION IV

CATHODIC CURVE

ANODIC CURVE

Ecorr

$\log i_{corr}$

$\log i$
4.2 POLARIZATION V

\[ E \]

\[ \text{CATHODIC CURVE} \]

\[ E_{\text{corr}} \]

\[ \text{ANODIC CURVE} \]

\[ I_{\text{corr}} \]

\[ I \]
4.3 WAGNER AND TRAUD’S SUPERPOSITION PRINCIPLE I

- IN A HOMOGENEOUS SURFACE WITH MULTIPLE REACTIONS WITH CURRENT DENSITIES $i_{ia}$

\[ i_{ic} \]

\[ i_{aT} = \sum i_{ia} = - \sum i_{ic} = - i_{cT} \]
4.3 WAGNER AND TRAUD’S SUPERPOSITION PRINCIPLE II

• SPECIAL CASE

SINGLE METAL DISSOLUTION COUPLED WITH A SINGLE CATHODIC REACTION

\[ M = M^+ + e \]

\[ i_a = -i_c = i_{corr} \]
4.3 WAGNER AND TRAUD’S SUPERPOSITION PRINCIPLE III

\[ i_{\text{corr}} = i_{oa} \{ \exp(\alpha_{aa} F [\phi^* - \phi_{oa}]/RT) - \exp(-\alpha_{ac} F [\phi^* - \phi_{oa}]/RT) \} = \]

\[ - i_{oc} \{ \exp(\alpha_{ca} F [\phi^* - \phi_{oc}]/RT) - \exp(-\alpha_{cc} F [\phi^* - \phi_{oc}]/RT) \} \]
4.3 WAGNER AND TRAUD’S SUPERPOSITION PRINCIPLE IV

• IN A COMPOSITE SURFACE (POLYELECTRODE) CONSISTING OF MANY AREAS $A_i$ WITH CURRENT DENSITIES $i_{ia}$ $i_{ic}$

\[ I_{aT} = \sum i_{ia} A_i = - \sum i_{ic} A_i = - I_{cT} \]
4.4 STERN AND GEARY’S ANALYSIS I

- WHEN THE EQUILIBRIUM POTENTIALS FOR THE TWO REACTIONS ARE WIDELY SEPARATED, THE BACK REACTION FOR EITHER OR BOTH REACTIONS MAY BE NEGLIGIBLE (TAFEL BEHAVIOR)
4.4 STERN AND GEARY’S ANALYSIS II

\[ i_{\text{corr}} = i_{oa} \exp(\alpha_{aa} F [\phi^* - \phi_{oa}] / RT) \]
\[ = i_{oc} \exp(-\alpha_{cc} F [\phi^* - \phi_{oc}] / RT) \}

AND

\[(\alpha_{aa} + \alpha_{cc}) \phi^* = (RT/F) \ln (i_{oc} / i_{oa}) + \alpha_{cc} \phi_{oc} + \alpha_{aa} \phi_{oa}\]
4.4 STERN AND GEARY’S ANALYSIS III

• THE TOTAL (NET) CURRENT DENSITY IS

\[ i_{\text{net}} = i_a + i_c = \]

\[ i_{\text{corr}} \left\{ \exp(\alpha_{aa} F [\phi - \phi^*]/RT) - \exp(-\alpha_{cc} F [\phi - \phi^*]/RT) \right\} \]

• JUST LIKE BUTLER-VOLMER
4.4 STERN AND GEARY’S ANALYSIS IV

IF ON A FREELY CORRODING SPECIMEN ($\phi^*$), A SMALL OVERVOLTAGE IS APPLIED, THE POTENTIAL INCREASES BY $\Delta \phi$ AND THE NET CURRENT DENSITY INCREASES BY

$$\Delta i = \Delta \phi \left\{ \frac{(\beta_a + |\beta_c|)}{(\beta_a |\beta_c|)} \right\}$$
4.4 STERN AND GEARY’S ANALYSIS V

\[ \text{slope} = \beta_c \]

\[ \Delta i \]

\[ \Delta \phi \]

\[ E_{\text{corr}} \]

\[ i_{\text{corr}} \]

\[ \text{slope} = \beta_a \]
• Since

\[ \beta_a = \frac{b_a}{(2.303 \ i_{\text{corr}})} \]
\[ \beta_c = \frac{b_c}{(2.303 \ i_{\text{corr}})} \]

\[ i_{\text{corr}} = \frac{(\Delta i/\Delta \phi)}{(b_a + |b_c|)/(b_a |b_c|)} \]

\[ \Delta \phi/\Delta i = \text{POLARIZATION RESISTANCE} \]
4.5 EXAMPLES I

• THE EVANS SALT DROP EXPERIMENT
  – 3% NaCl SOLUTION IN H₂O
  – POTASCIUM FERRICYANIDE (BECOMES BLUE IN PRESENCE OF Fe²⁺)
  – PHENOLPLHTALEIN (BECOMES PINK IN PRESENCE OF ALKALI)
  – FINELY ABRADED Fe SURFACE

• FORMATION OF PINK-RUST-BLUE RINGS AFTER SOME TIME
4.5 EXAMPLES II

• EXERCISE: CONSTRUCT POLARIZATION CURVES FOR
  – Fe CORRODING IN ACID SOLUTION
  – Fe CORRODING IN BASIC SOLUTION
  – Zn CORRODING IN ACID SOLUTION
  – Zn CORRODING IN BASIC SOLUTION

• EXPLORE THE SENSITIVITY OF THE RESULTS
4.5 EXAMPLES III

• EXERCISE: ASSUMING

\[ \alpha_{aa} = \alpha_{ac} = \alpha_{ca} = \alpha_{cc} = 1/2 \]

FOR SINGLE METAL DISSOLUTION
COUPLED WITH A SINGLE
CATHODIC REACTION FIND AN
EXPRESSION FOR \( \phi \)
4.5 EXAMPLES IV

- **EXERCISE:** VERIFY THE GIVEN STERN&GEARY EXPRESSION FOR $i_{\text{net}}$
- **EXERCISE:** USE THE GIVEN STERN&GEARY EXPRESSION FOR $i_{\text{net}}$ USE THE GIVEN TO COMPUTE THE $\phi - \log i_{\text{net}}$ POLARIZATION CURVE FOR THE FOUR SYSTEMS IN EXAMPLES II ABOVE
4.5 EXAMPLES V

- DETERMINE THE CORROSION POTENTIALS AND CORROSION CURRENT DENSITIES FOR THE FOUR SYSTEMS IN EXAMPLE II ABOVE
4.5 EXAMPLES VI

• **EXERCISE:** VERIFY THE GIVEN EXPRESSIONS FOR $\beta_a$ AND $\beta_c$ IN THE STERN-GEARY ANALYSIS
4.5 EXAMPLES VII

- EXERCISE: USE CURVE FITTING TO OBTAIN POLYNOMIAL APPROXIMATIONS OF ANODIC POLARIZATION CURVES SHOWING PASSIVITY THEN APPLY THE WAGNER-TRAUB ANALYSIS TO DETERMINE THE COMPOSITE POLARIZATION CURVE
5 COMPLEX CORROSION SYSTEMS

5.1 GOVERNING EQUATIONS
5.2 BOUNDARY CONDITIONS
5.3 ANALYTICAL SOLUTIONS
5.4 NUMERICAL SOLUTIONS
5.5 EXAMPLES
5.1 GOVERNING EQUATIONS I

- **FLUX EQUATION**

\[
N_i = - (z_i u_i C_i F/RT) \text{ grad } \phi - D_i \text{ grad } C_i + v C_i
\]

WHERE

- \( u_i \) IS THE IONIC MOBILITY
- \( v \) IS THE FLUID VELOCITY
5.1 GOVERNING EQUATIONS II

- CURRENT DENSITY EQUATION
  \[ i = F \Sigma z_i N_i \]

- MATERIAL BALANCE
  \[ \delta C_i / \delta t = - \text{div } N_i \]

- ELECTRONEUTRALITY CONDITION
  \[ \Sigma z_i C_i = 0 \]
5.1 GOVERNING EQUATIONS III

- NAVIER-STOKES EQUATIONS
  \[ \rho \frac{\partial v}{\partial t} + \left[ v \cdot \nabla \right] v = - \nabla p + \mu \nabla^2 v + \rho g \]

- CONTINUITY EQUATION
  \[ \text{div} \ v = 0 \]
5.1 GOVERNING EQUATIONS IV

• SIMPLIFICATIONS FOR POTENTIAL THEORY
  – WHEN CONCENTRATION GRADIENTS, ARE NOT IMPORTANT
    \[ i = - \kappa \text{grad} \phi \]
  – WHERE \( \kappa \) IS THE CONDUCTIVITY OF THE SOLUTION
5.1 GOVERNING EQUATIONS V

- SIMPLIFICATIONS FOR POTENTIAL THEORY (contd)
  - FROM THE MASS BALANCE EQUATION
    \[ \text{div grad } \phi = 0 \]

LAPLACE’S EQUATION
5.2 BOUNDARY CONDITIONS I

• FLUX NORMAL TO ELECTRODE SURFACE
  \[ N_{in} = - \left( \nu_i/zF \right) i_n = f(\eta_s, C_i) \]

• NO-SLIP AT FLUID-SOLID BOUNDARIES
  \[ v_f = v_s \]
5.2 BOUNDARY CONDITIONS II

- INSULATING BOUNDARIES
  \[ \frac{d\phi}{dn} = 0 \]

- CONDUCTING BOUNDARIES (POTENTIAL PROBLEMS)
  \[ \frac{d\phi}{dn} = \frac{i}{\kappa} \]
5.3 ANALYTICAL SOLUTIONS I

- ANALYTICAL SOLUTIONS OF POTENTIAL PROBLEMS ARE POSSIBLE IN A FEW SELECTED CASES

- ANALYTICAL SOLUTIONS CAN BE OBTAINED BY FOURIER SERIES OR CONFORMAL MAPPING METHODS
5.3 ANALYTICAL SOLUTIONS II

• WABER SOLUTION: GALVANIC SYSTEM AS BEFORE \( x_1 = 0, x_2 = a \) AND \( x_3 = c \) AND \( \phi = E_a \) ON 1-2 AND \( \phi = 0 \) ON 2-3

\[
\phi(x,y) = E_a \left( \pi \frac{a}{c} \right) + \left( 2 \frac{E_a}{\pi} \right) \\
\sum \left( \frac{1}{n} \right) e^{-n \pi \frac{y}{c}} \sin(n \pi \frac{a}{c}) \cos(n \pi \frac{x}{c})
\]
5.3 ANALYTICAL SOLUTIONS II

• AVAILABLE ANALYTICAL SOLUTIONS SHOULD BE USED AS REFERENCE FOR NUMERICAL WORK
5.4 NUMERICAL SOLUTIONS I

• DISCRETIZED VERSIONS OF THE MODELING EQUATIONS ARE SOLVED USING COMPUTERS

• DISCRETIZATION METHODS
  – FINITE DIFFERENCES
  – CONTROL VOLUME (BOX) METHOD
  – FINITE ELEMENTS
  – BOUNDARY ELEMENTS
5.4 NUMERICAL SOLUTIONS II

• FINITE DIFFERENCE METHOD FOR POTENTIAL PROBLEMS

1.- SUBDIVIDE THE DOMAIN OF INTEREST INTO A LATTICE OF MESH POINTS OR NODES

2.- REPLACE DERIVATIVES IN THE LAPLACE’S EQUATION FOR $\phi$ BY FINITE DIFFERENCES
5.4 NUMERICAL SOLUTIONS III

• FINITE DIFFERENCE METHOD FOR POTENTIAL PROBLEMS (contd)

3.- CREATE APPROPRIATE DISCRETE EQUATIONS FOR THE BOUNDARIES

4.- SOLVE RESULTING SET OF SIMULTANEOUS ALGEBRAIC EQUATIONS BY ITERATION
5.5 EXAMPLES I

- GALVANIC CORROSION

![Diagram showing galvanic corrosion with metal A and metal B in an electrolyte]
5.5 EXAMPLES II

- GALVANIC CORROSION (contd)
  - ELECTROLYTE (LAPLACE’S EQUATION)
    \[ \frac{\delta^2 \phi}{\delta x^2} + \frac{\delta^2 \phi}{\delta y^2} = 0 \]
  - BOUNDARIES 3-4, 5-1
    \[ \frac{\delta \phi}{\delta x} = 0 \]
5.5 EXAMPLES III

• GALVANIC CORROSION (contd)
  – BOUNDARY 4-5
    \[
    \frac{\delta \phi}{\delta y} = 0
    \]
  – BOUNDARY 1-2
    \[
    \frac{\delta \phi}{\delta y} = \frac{i_A}{\kappa}
    \]
  – BOUNDARY 2-3
    \[
    \frac{\delta \phi}{\delta y} = \frac{i_B}{\kappa}
    \]
5.5 EXAMPLES IV

- GALVANIC CORROSION (contd)
- FINITE DIFFERENCE FORMULAE (ELECTROLYTE; INTERIOR NODES)

\[
\frac{(\phi_E + \phi_W - 2 \phi_P )}{\Delta x^2} + \frac{(\phi_N + \phi_S - 2 \phi_P )}{\Delta y^2} = 0
\]
5.5 EXAMPLES V

INTERIOR NODES

\[ \Delta y, \Delta x \]

\[ P \]

\[ W, S, N, E \]
5.5 EXAMPLES VI

- **FINITE DIFFERENCE FORMULAE**
  (BOUNDARY NODES; BOUNDARY 1-2-3)

\[
\phi_p = \left[\frac{1}{2(1+\lambda^2)}\right] \left\{ (\phi_E + \phi_W) \lambda^2 + 2 \phi_N + \left( \frac{2\Delta y}{\kappa} \right) i \right\}
\]

**WITH** \( \lambda = \frac{\Delta y}{\Delta x} \)
5.5 EXAMPLES VII

• FINITE DIFFERENCE FORMULAE (BOUNDARY NODES; BOUNDARY 3-4)

\[
\phi_P = \left[ \frac{1}{2(1+(1/\lambda^2))} \right]
\]

\[
\{(\phi_N + \phi_S)(1/\lambda^2) + 2\phi_E\}
\]
5.5 EXAMPLES VIII

BOUNDARY NODES
5.5 EXAMPLES IX

• SOLUTION BY SUCCESSIVE OVER-RELAXATION ITERATION FOR ALL MESH POINTS. SOR EQUATION FOR MESH POINT \( i \) IS

\[
\phi_i^{n+1} = \phi_i^n + \left( \frac{\omega}{a_{ii}} \right) \left\{ b_i - \sum a_{ij} \phi_j^{n+1} - \sum a_{ij} \phi_j^n \right\}
\]

• WHERE \( \omega = \text{RELAXATION FACTOR} \)
5.5 EXAMPLES X

- EXERCISE: DERIVE THE FINITE DIFFERENCE FORMULAE GIVEN
- EXERCISE: DERIVE THE S.O.R. FORMULAE GIVEN
- EXERCISE: EXPLORE THE SENSITIVITY OF THE GALVANIC SYSTEM
REFERENCES I

- West, “Corrosion y Oxidacion: Fundamentos”, Limusa, Mexico, 1986
REFERENCES II

REFERENCES III