ELECTROCHEMISTRY AND CORROSION SCIENCE
— SOLUTION MANUAL –

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CHAPTERS:

Chapter 1

FORMS OF CORROSION

1.1 QUESTIONS

1.1 During metallic corrosion there is loss of weight of the metal. Why metals undergo corrosion in a suitable environment?

Answer: Metals are thermodynamically unstable in their free state and consequently, they corrode forming a metallic compound due to their reactivity in the surrounding environment.

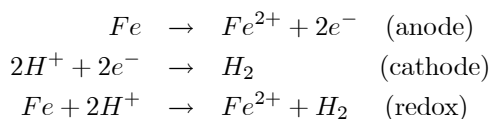**1.2** Is copper corrosion an oxidation process?

Answer: Corrosion is an oxidation process in which a pure metal surface reacts with its environment by loosing electrons, $Cu \rightarrow Cu^{2+} + 2e^-$, and forming a green film on the surface of copper.

1.3 It is known that corrosion on the surface of a metal is due to a direct reaction of atmospheric gases. Which gas is mainly responsible for the corrosion of most metallic iron and steel surfaces?
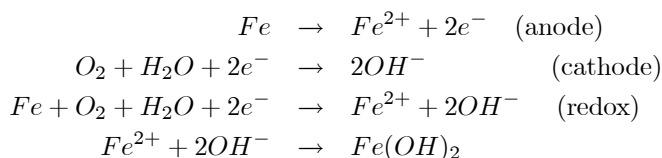
Answer: Oxygen when compared to halogens, oxides of sulphur, oxides of nitrogen, hydrogen sulphide.

1.4 What are the two mechanisms for oxidation of iron? Write down the suitable electrochemical reactions.

Answer: (a) In the absence of oxygen, the evolution of hydrogen in acid solutions (H_2) is represented by the following electrochemical reactions

$$
\begin{aligned}
Fe &\rightarrow Fe^{2+} + 2e^- \quad \text{(anode)} \\
2H^+ + 2e^- &\rightarrow H_2 \quad \text{(cathode)} \\
Fe + 2H^+ &\rightarrow Fe^{2+} + H_2 \quad \text{(redox)}
\end{aligned}
$$

(b) Absorption of oxygen (O_2) in neutral or basic medium.

$$\begin{aligned}
Fe &\rightarrow Fe^{2+} + 2e^- \quad \text{(anode)} \\
O_2 + H_2O + 2e^- &\rightarrow 2OH^- \quad\quad\quad \text{(cathode)} \\
Fe + O_2 + H_2O + 2e^- &\rightarrow Fe^{2+} + 2OH^- \quad \text{(redox)} \\
Fe^{2+} + 2OH^- &\rightarrow Fe(OH)_2
\end{aligned}$$

1.5 Investigate the differences between dry and wet corrosion Write down at least three differences per type of corrosion.
Solution:

Dry Corrosion
1. Corrosion occurs in the absence of moisture
2. Chemicals in the dry environment attack the metal surface
3. It is a slow process

Wet Corrosion
1. Corrosion occurs in presence of moisture
2. It involves formation of electrochemical cells
3. It is a fast process.

1.6 What is bimetallic corrosion?
Answer: It is an electrochemical corrosion due to dissimilar metals being connected and exposed to an electrolyte, forming a galvanic cell.

1.7 What form of corrosion will cause sand grains, dust particles and an oxide scale on the surface of metals exposed to a corrosive medium?
Answer: Pitting corrosion.

1.8 Why stress corrosion is not uniform?
Answer: Stress corrosion not uniform because a mechanically stressed structure is highly strained at certain locations, which become the localized anodic sites for corrosion to take place there.

1.9 What form of corrosion develops at rivets and bolts?
Answer: Crevice corrosion

1.10 Corrosion is a process of destruction of a metal surface by the surrounding environment. Environmental parameters like temperature, humidity, gases (CO_2, SO_2, NO_x) and pH. play an important role in studying corrosion. What are the two factors that govern the corrosion process?
Answer: Metallic and environmental

1.11 What are the main effects or consequences of corrosion of structures?
Answer: To name a few

- Corrosion reduces the thickness of metal parts of a structure and as result, loss of mechanical strength occurs, leading failure of the structure.

- Efficiency of machines is reduced due to corrosion.

- Because of corrosion, pipes, boilers and pumps are blocked by the corrosion compound and therefore, they are difficult to operate efficiently.

1.12 The principle constituent of wood is cellulose, which is a polysaccharide. This is a polymer made of sugar molecules joined in long chains. Will these sugar molecules corrode a galvanized steel nail and weaken a wood beam in a hypothetical fishing vessel?

Answer: Anodic coating is used as a sacrificial material during a certain period of time and cathodic coating is used as a cathodic protection technique.

1.13 What method is used to prevent corrosion of iron by zinc coating?
Answer: Galvanisation

1.14 The principle constituent of wood is cellulose, which is a polysaccharide. This is a polymer made of sugar molecules joined in long chains. Will these sugar molecules corrode a galvanized steel nail and weaken a wood beam in a hypothetical fishing vessel?

Answer: The galvanized steel nail will corrode and the corrosion product will soften the wood beam at contact

with the nail. Consequently, the vessel will begin to lose structural stability.

Chapter 2

ELECTROCHEMISTRY

2.1 PROBLEMS/QUESTIONS

2.1 Define the galvanic electrode potential for the cell shown in Figure 2.4 using the interfacial potentials involved in the electrochemical process.

Solution:

$$
\begin{aligned}
E &= \left[\phi_{Cu} - \phi_{Cu\,SO_4}\right]_{Half-cell} + \left[\phi_{Zn\,SO_4} - \phi_{Zn}\right]_{Half-cell} \\
&\quad + \left[\phi_{Cu\,SO_4} - \phi_{Zn\,SO_4}\right] + \left[\phi_{Zn} - \phi'_{Cu}\right]_{Wire} + \left[\phi_{Cu} - \phi''_{Cu}\right]_{Wire} \\
&\quad + \left[\phi_{Cu\,SO_4} - \phi_{Zn\,SO_4}\right]_{Bridge} \\
E &= \phi_{Cu} + \phi_{Cu\,SO_4} - \phi_{Cu\,SO_4} + \phi_{Zn\,SO_4} - \phi_{Zn\,SO_4} + \phi_{Zn} - \phi_{Zn} - \phi'_{Cu} \\
&\quad + \phi_{Cu} - \phi''_{Cu} \\
E &= \phi_{Cu} - \phi'_{Cu}
\end{aligned}
$$

since $\phi_{Cu} = \phi''_{Cu}$ at the copper electrode and copper wire junction. In addition, let ϕ'_{Cu} and ϕ''_{Cu} be the potential at the copper wire-zinc electrode and the potential at copper wire-copper electrode junctions, respectively.

2.2 Described what happens in the galvanic cell shown in Figure 2.4 when electrons leave the Cu terminal at the Cu-Zn interface.

Explanation: *The $Cu - Zn$ interface is disturbed causing electrons to flow out of Zn into Cu terminal and consequently, Zn oxidizes according to the anodic reaction $Zn = Zn^{+2} + 2e$. This reaction occurs at the Zn-$ZnSO_{4(aq.)}$ interface where Zn^{+2} cations go into solution loosing electrons. Then, these electrons react with Cu^{+2} cations according to the cathodic reaction $Cu^{+2} + 2e = Cu$.*

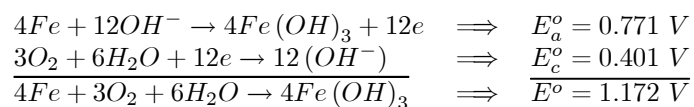**2.3** Explain why an electrode potential difference occurs in Figure 2.4.

Explanation: *The $CuSO_4$ solution is depleted of Cu^{+2} cations and the $ZnSO_4$ is enriched in Zn^{+2} cations. This causes a flow of positive ions (cations) through the solutions from the Zn electrode to the Cu electrode and a flow of negative SO_4^{-2} ions (anions) towards the Zn electrode. Hence, the current is carried through the solution by these ions.*

2.4 Why are Cu^{+2} cations electroplated on the Cu electrode surface in Figure 2.4?

Answer: *During the operation of the galvanic cell both $Zn \rightarrow Zn^{+2} + 2e$ and $Cu^{+2} + 2e \rightarrow Cu$ reactions occur since the electron flow process is $2e\,(Zn) \rightarrow 2e\,(Cu)$ and Cu^{+2} is reduced on the Cu electrode surface as a metallic element.*

2.5 Calculate the standard potential for the formation of ferric hydroxide $Fe(OH)_3$ (brown rust).

Solution: *The possible half-cell reactions and their respective standard potential are*

$$
\begin{array}{lll}
4Fe + 12OH^- \rightarrow 4Fe\,(OH)_3 + 12e & \implies & E_a^o = 0.771\ V \\
3O_2 + 6H_2O + 12e \rightarrow 12\,(OH^-) & \implies & E_c^o = 0.401\ V \\
\hline
4Fe + 3O_2 + 6H_2O \rightarrow 4Fe\,(OH)_3 & \implies & E^o = 1.172\ V
\end{array}
$$

The standard potentials were taken from Table 2.3. *Thus, $E^o = E_a^o + E_c^o = 1.172\ V$.*

2.6 Explain why care must be exercised in using the galvanic series illustrated in Table 2.2.

Explanation: *The electrode anodic and cathodic reactions dissipate energy and consequently, the electrode potentials and activities may be altered.*

2.7 If zinc and copper rods are placed in salt water, a direct chemical reaction may slightly corrode zinc. Why?

Answer: *Because Zn is more active than Cu and therefore, Zn is anodic to Cu.*

2.8 Is the cell potential a surface potential? If so, why?

Answer: *E_{corr} must be a surface potential because it arises due to simultaneous anodic and cathodic reactions on the metal surface.*

2.9 If a monopole contains a net charge (Q) due to 10^{-12} moles of a species j in a electrically neutral system, then calculate the electric potential (ϕ_x), the electric potential strength (E_x) and the electric force (F_x) acting on a particle within a distance of 9 cm from another charged particle in the x-direction.

Solution:

From eq. (2.4),

$$\begin{aligned} Q &= zFX = (2)(96,500 \text{ C}/mol)\left(10^{-12} \text{ } mol\right) \\ Q &= 1.93x10^{-7} \text{ C} = 0.193 \text{ } \mu C \end{aligned}$$

But,

$$\begin{aligned} \lambda &= \frac{1}{4\pi\epsilon_o} = 9x10^9 \text{ } \frac{\text{N.m}^2}{\text{C}^2} = 9x10^9 \text{ } \frac{\text{J.m}}{\text{C}^2} \\ r &= 0.09 \text{ m} \end{aligned}$$

Inserting these values into eq. (2.8) give the magnitude of the electric potential on a monopole system. Thus,

$$\begin{aligned} \phi_x &= \frac{\lambda Q}{r} = \frac{\left(9\times10^9 \text{ J.m/ C}^2\right)\left(1.93x10^{-7} \text{ C}\right)}{0.09 \text{ m}} \\ \phi_x &= 19,300 \text{ } J/C = 19,300 \text{ } N.m/C \\ \phi_x &= 19,300 \text{ } J/(J/V) = 19,300 \text{ } V = 19.30 \text{ } kV \end{aligned}$$

which is a high value for the isolated monopole case. The magnitude of the electric potential strength is expected to have a very high magnitude given by eq. (2.17). Thus,

$$\begin{aligned} E_x &= \frac{\lambda Q}{r^2} = \frac{\phi}{r} = \frac{19,300 \text{ } N.m/C}{0.09 \text{ } m} \\ E_x &= 2.14\times10^5 \text{ } N/C = 2.14\times10^5 \text{ } V/m \end{aligned}$$

Thus, the electric force acting on the particle becomes

$$\begin{aligned} F_x &= QE_x = \left(1.93x10^{-7} \text{ } C\right)\left(2.14\times10^5 \text{ } N/C\right) \\ F_x &= 0.04 \text{ } N \end{aligned}$$

2.10 A battery (Example 2.2) containing 0.4 moles of MnO_2 delivers 1.5 V. For 4-hour operation, calculate the electric current and the power (in watts).

Solution:

From example 2.2, $MnO_2 + H^+ + e \rightarrow MnOOH$ *and*

$$
\begin{aligned}
Q &= zFX_{MnO_2} = (1)(96500 \ A.s/mol)(0.4 \ mol) \\
Q &= 38,600 \ A.s = 38,600 \ C = 38.60 \ kJ/V
\end{aligned}
$$

Then,

$$
\begin{aligned}
I &= \frac{Q}{t} = \frac{38,600 \ A.s}{4 \times 60 \times 60 \ s} = 2.68 \ A \\
P &= EI = (1.5 \ V)(2.68 \ A) = 4.02 \ V.A = 4.02 \ watts
\end{aligned}
$$

2.11 Write down the reversible hydrogen reaction for a standard electrode and determine its standard electric potential.

Solution:

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

The standard electric potential for the above reaction is taken a zero because it is a standard reference. Thus, $E^o_{H_2/H^+} = 0$.

2.12 Calculate the E^o values for each of the following reactions as written and determine which one is the cathode and anode.
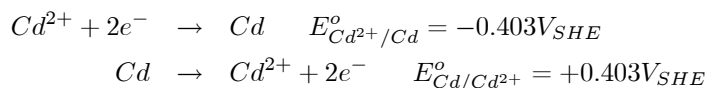
$$
2Fe^{3+} + Cd \rightarrow Cd^{2+} + 2Fe^{2+}
$$
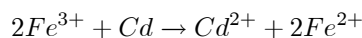
Solution:
From Table 2.2,

$$
\begin{aligned}
E^o &= E^o_{Fe^{3+}/Fe^{2+}} + E^o_{Cd/Cd^{2+}} = 0.77 \ V_{SHE} + 0.403 \ V_{SHE} \\
E^o &= 1.173 \ V_{SHE} \\
Fe^{+3} &= \text{Cathode because it reduces to } Fe^{+2} \\
Cd &= \text{Anode because it oxidizes to } Cd^{2+}
\end{aligned}
$$

Recall that the reactions illustrated in Table 2.2 are for reduction processes. In this problem cadmium (Cd) oxidizes and therefore, the standard potential changes its sign from negative to positive. That is,
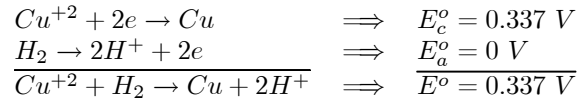
$$
\begin{aligned}
Cd^{2+} + 2e^- &\rightarrow Cd & E^o_{Cd^{2+}/Cd} &= -0.403 V_{SHE} \\
Cd &\rightarrow Cd^{2+} + 2e^- & E^o_{Cd/Cd^{2+}} &= +0.403 V_{SHE}
\end{aligned}
$$

Chapter 3

THERMODYNAMICS OF AN ELECTROCHEMICAL CELL

3.1 PROBLEMS

3.1 Consider the following electrochemical cell $\left|Cu^{+2}, Cu\right| \left|H_2, H^+\right| Pt$ to calculate the maximum activity of copper ions Cu^{+2} in solution due to oxidation of a copper strip immersed in sulfuric acid H_2SO_4 at $25\,^\circ$C, $101\ kPa$ and $pH = 2$.

Solution: *The possible half-cell reactions and their respective standard potentials* (Table 2.2) *are*

$$
\begin{array}{lll}
Cu^{+2} + 2e \to Cu & \implies & E_c^o = 0.337\ V \\
H_2 \to 2H^+ + 2e & \implies & E_a^o = 0\ V \\
\hline
Cu^{+2} + H_2 \to Cu + 2H^+ & \implies & E^o = 0.337\ V
\end{array}
$$

Then,

$$
\begin{aligned}
\Delta G^o &= -zFE^o = (2)\left(96,500\ \frac{J}{mol.V}\right)(0.337\ V) \\
\Delta G^o &= -65\ \frac{kJ}{mol}
\end{aligned}
$$

Therefore, the reactions will occur as written since $\Delta G^o < 0$. The maximum activity of Cu^{+2} cations can be calculated when the potential and current densities are $E_{Cu} = E_H$ at $i_{corr} = i_{\max}$. Using the Nernst equation yields

$$E_{Cu} = E_{Cu}^o - \frac{RT}{zF} \ln \frac{[Cu]}{[Cu^{+2}]}$$

$$E_H = E_H^o - \frac{RT}{zF} \ln \frac{[H^+]^2}{[H_2]} = -0.059pH$$

$$E_H = -0.059\,(2) = -0.118 \ V$$

Letting $E_{Cu} = E_H = -0.118 \ V$ yields

$$E_H = E_{Cu}^o - \frac{RT}{zF} \ln \frac{[Cu]}{[Cu^{+2}]} = -0.118 \ V$$

$$\ln \frac{[Cu]}{[Cu^{+2}]} = (E_{Cu}^o - E_H)\left(\frac{zF}{RT}\right)_{Cu}$$

$$\left(E_{Cu}^o - E_H\right)\left(\tfrac{zF}{RT}\right)_{Cu} = (0.337 \ \mathrm{V} + 0.118 \ \mathrm{V}) \left[\frac{(2)\left(96500 \ \frac{\mathrm{J}}{\mathrm{mol.V}}\right)}{\left(8.314 \ \frac{\mathrm{J}}{\mathrm{mol.^oK}}\right)(298 \ ^o\mathrm{K})} \right]$$

$$\left(E_H - E_{Cu}^o\right)\left(\frac{zF}{RT}\right)_{Cu} = 35.44$$

and

$$\ln \frac{[Cu]}{[Cu^{+2}]} = 35.44$$

$$\frac{[Cu]}{[Cu^{+2}]} = 2.46x10^{15}$$

Thus,

$$\left[Cu^{+2}\right] = \frac{[Cu]}{2.46x10^{15}} = \frac{1 \ mol/l}{2.46x10^{15}}$$

$$a_{Cu^{+2}} = \left[Cu^{+2}\right] = 4.06x10^{-16} \ mol/l$$

3.2   Consider a galvanic cell $| \ Zn\,|0.10MZnSO_4|\,|0.10 \ M \ NiSO_4|\,Ni \ |$. Calculate the cell potential using the Nernst equation at $T = 25\,^\circ$C.

Solution: *The possible half-cell reactions and their respective standard potential* (Table 2.2*) are*
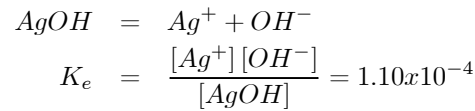
$$
\begin{array}{lll}
Ni^{+2} + 2e \rightarrow Ni & \Longrightarrow & E_{Ni}^o = -0.250 \ V \\
\underline{Zn \rightarrow Zn^{+2} + 2e} & \Longrightarrow & \underline{E_{Zn}^o = +0.763 \ V} \\
Ni^{+2} + Zn \rightarrow Ni + Zn^{+2} & \Longrightarrow & E = +0.513 \ V
\end{array}
$$
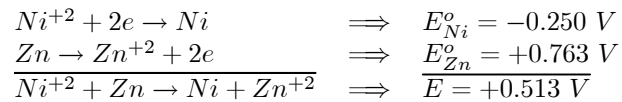
Using the Nernst equation along with $\left[Ni^{+2}\right] = \left[Zn^{+2}\right] = 0.10 \ mol/l$ and $[Ni] = [Zn] = 1 \ mol/l$ gives

$$
\begin{aligned}
E_{Ni} &= E^o_{Ni} - \frac{RT}{zF} \ln \frac{[Ni]}{[Ni^{+2}]} = -0.280 \ V \\
E_{Zn} &= E^o_{Zn} - \frac{RT}{zF} \ln \frac{[Zn^{+2}]}{[Zn]} = 0.793 \ V \\
E &= E_{Ni} + E_{Zn} = 0.513 \ V
\end{aligned}
$$

3.3 The dissociation constant of silver hydroxide, $AgOH$, is $1.10x10^{-4}$ at $25\,^{\circ}C$ in an aqueous solution. (a) Write down the chemical reaction and (b) determine the Gibbs free energy change ΔG^o.

Solution:

(a) *The dissociation chemical reaction is*

$$
\begin{aligned}
AgOH &= Ag^+ + OH^- \\
K_e &= \frac{[Ag^+][OH^-]}{[AgOH]} = 1.10x10^{-4}
\end{aligned}
$$

(b) *The free energy change is*

$$
\begin{aligned}
\Delta G^o &= -RT \ln (K_e) = - \left(8.314 \ \frac{J}{mol.^oK} \right) (298^oK) \ln \left(1.1x10^{-4}\right) \\
\Delta G^o &\approx -22.58 \ kJ/mol
\end{aligned}
$$

Therefore, the reaction will proceed as written since $\Delta G^o < 0$.

3.4 Calculate (a) the concentration of $AgOH$ and Ag^+ in g/l at $25\,^{\circ}C$ and (b) the pH if $[OH^-] = 4.03x10^{-3} \ mol/l$ and $K_e = 1.10x10^{-4}$.

Solution:

(a) $AgOH = Ag^+ + OH^-$ *and* $K_e = 1.10x10^{-4}$. *Let* $[Ag^+] = [OH^-]$ *for charge balance so that*

$$
\begin{aligned}
K_e &= \frac{[Ag^+][OH^-]}{[AgOH]} = \frac{[OH^-]^2}{[AgOH]} \\
[AgOH] &= \frac{[OH^-]^2}{K_e} = \frac{\left(4.03 * 10^{-3}\right)^2}{1.10 * 10^{-4}} = 0.15 \ mol/l
\end{aligned}
$$

But,

$$\begin{aligned}
C_{AgOH} &= [AgOH]\, A_{w,AgOH} \\
C_{AgOH} &= (0.15\ mol/l)\left(107.87\ \tfrac{g}{l}\right) = 18.73\ g/l \\
[Ag^+] &= [OH^-] = 4.03x10^{-3}\ mol/l \\
C_{Ag^+} &= [Ag^+]\, A_{w,Ag} = \left(4.03x10^{-3}\ \tfrac{mol}{l}\right)\left(107.87\ \tfrac{g}{l}\right) = 0.43\ g/l \\
C_{OH^-} &= [OH^-]\, A_{w,OH} = \left(4.03x10^{-3}\ \tfrac{mol}{l}\right)\left(17\ \tfrac{g}{mol}\right) = 6.85x10^{-2}\ g/l
\end{aligned}$$

(b) *The dissociation of water ant its rate constant are*

$$\begin{aligned}
H_2O &= H^+ + OH^- \\
K_w &= \frac{[H^+]\,[OH^-]}{[H_2O]} = 10^{-14}
\end{aligned}$$

where $[H_2O] = 1\ mol/l$ *and*

$$\begin{aligned}
[H^+] &= \frac{K_w}{[OH^-]} = \frac{10^{-14}}{4.03x10^{-3}\ mol/l} = 2.48x10^{-12}\ mol/l \\
pH &= -\log[H^+] = -\log\left(2.48x10^{-12}\right) = 11.61
\end{aligned}$$

3.5 For an electrochemical copper reduction reaction at $25\,^\circ C$ and $101\ kPa$, calculate **(a)** the Gibbs free energy change ΔG^o as the driving force, **(b)** the equilibrium constant K_e and **(c)** the copper ion concentration $[Cu^{+2}]$ in g/l.

Solution:

(a) *The reduction reaction and its standard potential are*

$$Cu^{+2} + 2e = Cu \quad E^o = 0.337\ V$$
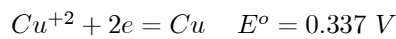
$$\begin{aligned}
\Delta G^o &= -zFE^o = -(2)\left(96,500\ \frac{J}{mol.V}\right)(0.337\ V) \\
\Delta G^o &= -65,041\ \frac{J}{mol}
\end{aligned}$$

(b) *The equilibrium constant is*

$$\begin{aligned}
\ln K_e &= -\frac{\Delta G^o}{RT} = -\frac{\left(-65,041\ \frac{J}{mol}\right)}{\left(8.314\ \frac{J}{mol.^\circ K}\right)(298\ ^\circ K)} = 26.25 \\
K_e &= 2.52x10^{11}
\end{aligned}$$
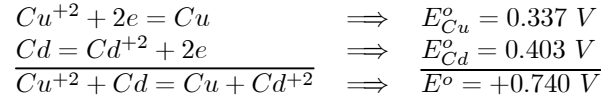
(c) *The concentration of copper cations is*

$$K_e = \frac{[Cu]}{[Cu^{+2}]}$$

$$[Cu^{+2}] = \frac{[Cu]}{K_e} = \frac{1 \ mol/l}{2.52x10^{11}} = 3.97x10^{-12} \ mol/l$$

$$C_{Cu^{+2}} = [Cu^{+2}] A_{w,Cu} = (3.97x10^{-12} \ mol/l) (63.55 \ g/mol)$$

$$C_{Cu^{+2}} = 2.52x10^{-10} g/l$$

3.6 Use the electrochemical cell $| \ Cd \ |0.05 \ M \ Cd^{+2}| \ |0.25 \ M \ Cu^{+2}| \ Cu \ |$ to calculate a) the temperature for an electric potential of $0.762 \ V_{SHE}$, and b) ΔS, ΔG, ΔH, and Q.

Solution:

a) *The reactions and the required temperature are*

$$
\begin{array}{lll}
Cu^{+2} + 2e = Cu & \Longrightarrow & E^o_{Cu} = 0.337 \ V \\
Cd = Cd^{+2} + 2e & \Longrightarrow & E^o_{Cd} = 0.403 \ V \\
\hline
Cu^{+2} + Cd = Cu + Cd^{+2} & \Longrightarrow & E^o = +0.740 \ V
\end{array}
$$

$$E = E^o - \frac{RT}{zF} \ln (K_e)$$

$$K_e = \frac{[Cu] [Cd^{+2}]}{[Cd] [Cu^{+2}]} = \frac{[1] [0.05]}{[1] [0.25]} = 0.2$$

$$T = -\frac{zF (E - E^o)}{R \ln (K_e)}$$

$$T = -\frac{(2) (96,500 \ \frac{J}{mol.V}) (0.762 \ V - 0.740 \ V)}{(8.314 \ \frac{J}{mol.^oK}) \ln (0.2)}$$

$$T = 317.32^o K = 44.32^o C$$

b) *Using eqs. (2.32) and (2.35) at constant pressure yields*

$$E = E^o - \frac{RT}{zF} \ln (K_e)$$

$$\frac{\partial E}{\partial T} = -\frac{R}{zF} \ln (K_e)$$

$$\Delta S = zF \frac{\partial E}{\partial T} = -R \ln (K_e)$$

$$\Delta S = - \left(8.314 \ \frac{J}{mol.^oK} \right) \ln (0.2) = 13.38 \ \frac{J}{mol.^oK}$$

From eq. (2.26),

$$\Delta G = -zFE = (2)\left(96,500 \ \frac{J}{mol.V}\right)(0.762 \ V)$$
$$\Delta G = -147 \ kJ/mol$$

From eq. (2.34),

$$\Delta H = \Delta G + T\Delta S$$
$$\Delta H = -147,000 \ J/mol + (317.32^o K)\left(13.38 \ \frac{J}{mol.^o K}\right)$$
$$\Delta H = 151.25 \ J/mol$$

From eq. (236),

$$Q = -T\Delta S = -(317.32^o K)\left(13.38 \ \frac{J}{mol.^o K}\right)$$
$$Q = -4.25 \ kJ/mol$$

3.7 Pure copper and pure cobalt electrodes are separately immersed in solutions of their respective divalent ions, making up a galvanic cell that yields a cell potential of 0.65 V_{SHE}. Calculate a) the cobalt activity if the activity of copper ions is 0.85 mol/l at 25 °C and b) the change in entropy ΔS^o and Gibbs free energy ΔG^o.

Solutions:

a) The reactions and the required cobalt activity are

$$\begin{array}{lll} Cu^{+2} + 2e = Cu & \Longrightarrow & E^o_{Cu} = 0.337 \ V \\ Co = Co^{+2} + 2e & \Longrightarrow & E^o_{Co} = 0.227 \ V \\ \hline Cu^{+2} + Co = Cu + Co^{+2} & \Longrightarrow & E^o = +0.614 \ V \end{array}$$
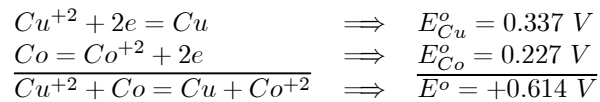
Using eq. (2.32) yields

$$E = E^o - \frac{RT}{zF}\ln(K_e)$$
$$\ln(K_e) = -\frac{zF(E - E^o)}{RT}$$
$$\ln(K_e) = -\frac{(2)\left(96,500 \ \frac{J}{mol.V}\right)(0.65 \ V - 0.614 \ V)}{\left(8.314 \ \frac{J}{mol.^o K}\right)(298^o K)} = -2.8044$$
$$K_e = 0.0605$$

Thus,

$$K_e = \frac{[Cu]\,[Co^{+2}]}{[Cu^{+2}]\,[Co]}$$

$$[Co^{+2}] = \frac{K\,[Cu^{+2}]\,[Co]}{[Cu]} = \frac{(0.0605)\,[0.85\ mol/l]\,[1\ mol/l]}{[1\ mol/l]}$$

$$a_{Co+2} = [Co^{+2}] = 0.0515\ mol/l$$

b) Using eqs. (2.32) and (2.35) at constant pressure yields

$$E = E^o - \frac{RT}{zF}\ln(K_e)$$

$$\frac{\partial E}{\partial T} = -\frac{R}{zF}\ln(K_e)$$

$$\Delta S = zF\frac{\partial E}{\partial T} = -R\ln(K_e)$$

$$\Delta S = -\left(8.314\ \frac{J}{mol.^oK}\right)\ln(0.0605) = 23.32\ \frac{J}{mol.^oK}$$

From eq. (2.26),

$$\Delta G = -zFE = -(2)\left(96,500\ \frac{J}{mol.V}\right)(0.65\ V)$$

$$\Delta G = -125.45\ kJ/mol$$

3.8 Show that the activities are $\left[M_1^{+2}\right] = \left[M_2^{+2}\right]$ in a galvanic cell, provided that the potentials is $E = E^o$.

Solution:

The reactions and the required activities are

$$M_1 = M_1^{+2} + 2e \qquad \Longrightarrow \quad E^o_{M_1}$$
$$\underline{M_{2+2} + 2e = M_2 \qquad \Longrightarrow \quad E^o_{M_2}}$$
$$M_1 + M_2^{+2} = M_1^{+2} + M_2 \quad \Longrightarrow \quad E^o = E^o_{M_1} + E^o_{M_2}$$

Using eq. (2.32) yields

$$E = E^o - \frac{RT}{zF}\ln\left(K_e\right)$$

$$\frac{dE}{dT} = \frac{R\ln\left(K_e\right)}{zF} = 0$$

$$\ln\left(K_e\right) = \ln\frac{\left[M_1^{+2}\right]}{\left[M_2^{+2}\right]} = 0$$

$$\ln\left[M_1^{+2}\right] - \ln\left[M_2^{+2}\right] = 0$$

$$\ln\left[M_1^{+2}\right] = \ln\left[M_2^{+2}\right]$$

$$\left[M_1^{+2}\right] = \left[M_2^{+2}\right]$$

3.9 Show that $\Delta S = -R\ln K_e$ in a galvanic cell at constant pressure.

Solution:

Using eqs. (2.32) and (2.35) at constant pressure yields

$$E = E^o - \frac{RT}{zF}\ln\left(K_e\right)$$

$$\frac{\partial E}{\partial T} = -\frac{R}{zF}\ln\left(K_e\right)$$

$$\Delta S = zF\frac{\partial E}{\partial T} = -R\ln\left(K_e\right)$$

3.10 Derive an expression for $\ln\left[Cu^{+2}\right] = f(T)$ for the given cells below. Assume that the current ceases to flow and that the cells are not replenished with fresh solutions. Plot the expressions for a temperature range of $0\,°\mathrm{C} \leq T \leq 60\,°\mathrm{C}$, and draw some suitable conclusions to explain the electrochemical behavior based on the resultant trend.
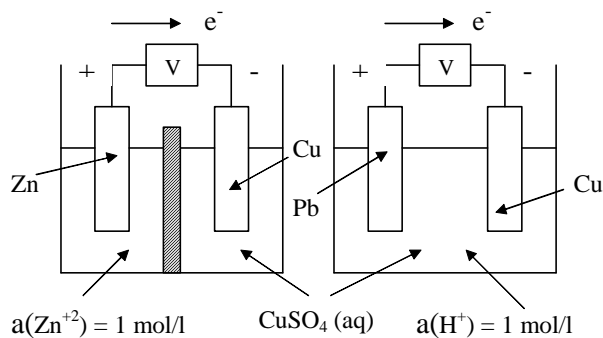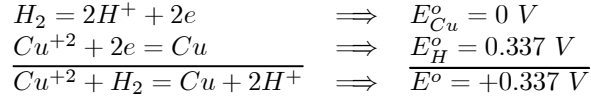

Solution:
a) *The reactions and the required copper activity are*

$$Cu^{+2} + 2e = Cu \qquad \Longrightarrow \qquad E^o_{Cu} = 0.337 \ V$$
$$Zn = Zn^{+2} + 2e \qquad \Longrightarrow \qquad E^o_{Zn} = 0.763 \ V$$
$$\overline{Cu^{+2} + Zn = Cu + Zn^{+2}} \quad \Longrightarrow \quad \overline{E^o = +1.10 \ V}$$
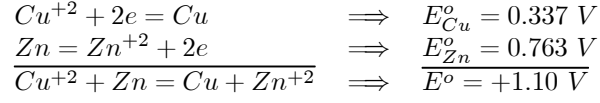
$$K_e \ = \ \frac{[Cu]\left[Zn^{+2}\right]}{\left[Cu^{+2}\right][Zn]} = \frac{[1][1]}{\left[Cu^{+2}\right][1]} = \frac{1}{\left[Cu^{+2}\right]}$$

$$E \ = \ E^o - \frac{RT}{zF}\ln\left(K_e\right) = 0$$

$$\ln\left(K_e\right) \ = \ \frac{zFE^o}{RT} =$$

$$\ln\frac{1}{\left[Cu^{+2}\right]} \ = \ \frac{zFE^o}{RT}$$

$$\ln\left[Cu^{+2}\right] \ = \ -\frac{zFE^o}{RT} - \frac{(2)\left(96,500 \ \frac{J}{mol.V}\right)(1.10 \ V)}{\left(8.314 \ \frac{J}{mol.^oK}\right)T}$$

$$\ln\left[Cu^{+2}\right] \ = \ -\frac{2.55x10^4}{T} = y \qquad (Solid \ curve)$$

b) *Similarly, the Pb-Cu Cell gives*

$$H_2 = 2H^+ + 2e \qquad \Longrightarrow \qquad E^o_{Cu} = 0 \ V$$
$$Cu^{+2} + 2e = Cu \qquad \Longrightarrow \qquad E^o_H = 0.337 \ V$$
$$\overline{Cu^{+2} + H_2 = Cu + 2H^+} \quad \Longrightarrow \quad \overline{E^o = +0.337 \ V}$$

$$K_e \ = \ \frac{[Cu]\left[Pb^{+2}\right]}{\left[Cu^{+2}\right][Pb]} = \frac{[1][1]}{\left[Cu^{+2}\right][1]} = \frac{1}{\left[Cu^{+2}\right]}$$

$$E \ = \ E^o - \frac{RT}{zF}\ln\left(K_e\right) = 0$$

$$\ln\left(K_e\right) \ = \ \frac{zFE^o}{RT}$$

$$\ln\frac{1}{\left[Cu^{+2}\right]} \ = \ \frac{zFE^o}{RT}$$

$$\ln\left[Cu^{+2}\right] \ = \ -\frac{zFE^o}{RT} - \frac{(2)\left(96,500 \ \frac{J}{mol.V}\right)(0.337 \ V)}{\left(8.314 \ \frac{J}{mol.^oK}\right)T}$$

$$\ln\left[Cu^{+2}\right] \ = \ -\frac{7823.1}{T} = y \qquad (Dash \ curve)$$

The required plots are $y = \ln\left[Cu^{+2}\right] = f\left(T\right)$
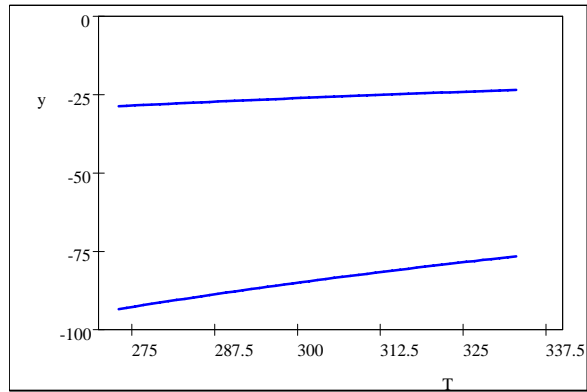
The plot below shows the trend of the derived expressions at a larger range.
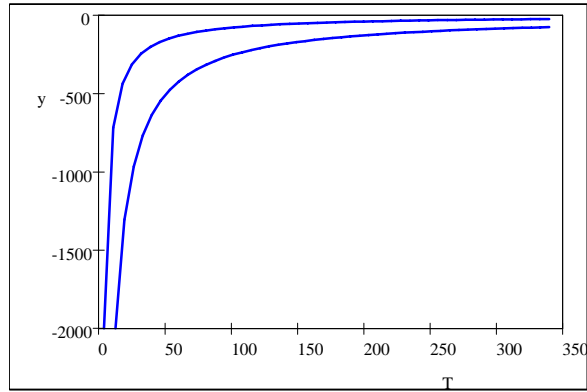
Besides the differences in activity behavior, either trend means that the activity, solution conductivity and ionic diffusivity increase with increasing temperature. In addition, the reduction of copper ions is faster at higher temperature.

EXTRA:

EX1. From Levine [2].

The entropy change (dS), the electrical energy change (dE), and the change of charge (dq) for a α-ϵ coupling are, respectively

$$dS = dS^\alpha + dS^\epsilon \tag{3.1a}$$

$$T^\alpha dS^\alpha = dU^\alpha + P^\alpha dV^\alpha - [(\mu^\alpha d\eta^\alpha)_M + (\mu^\alpha d\eta^\alpha)_e] \tag{3.1b}$$

$$T^\epsilon dS^\epsilon = dU^\epsilon + P^\epsilon dV^\epsilon - (\mu^\epsilon d\eta^\epsilon)_{M^{z+}} \tag{3.1c}$$

$$dE = dU^\alpha + dU^\epsilon + \phi^\alpha dq^\alpha + \phi^\epsilon dq^\epsilon \tag{3.1d}$$

$$dq = dq^\alpha + dq^\epsilon = z_e F (d\eta^\alpha)_e + zF (d\eta^\epsilon)_{M^{z+}} \tag{3.1e}$$

where μ = Chemical potential $\qquad$ P = Pressure $\qquad$ E = Total energy
$\qquad\quad\;\, U$ = Internal energy $\qquad\quad\;\, V$ = Volume
$\qquad\quad\;\, S$ = Entropy $\qquad\qquad\quad\; T$ = Temperature
$\qquad\quad\;\, q$ = Electron charge $\qquad\;\; \eta$ = Number of moles
$\qquad\quad\;\, \phi$ = Electric potential $\qquad\; F$ = Faraday's constant
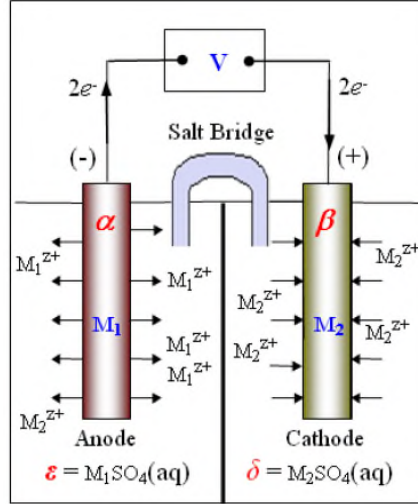
Figure 3.1 Galvanic cell and its phase components.

For an isolated α-ϵ thermodynamic system, the following constraints can be used to develop the equilibrium conditions and the Gibbs free energy change (ΔG) [2]

$$(d\eta^\alpha)_{M^{z+}} = -(d\eta^\alpha)_M \tag{3.2a}$$

$$dV^\epsilon = -dV^\alpha \tag{3.2b}$$

$$dV = 0 \tag{3.2c}$$

$$dE = 0 \tag{3.2d}$$

$$dq = 0 \tag{3.2e}$$

Hence, combining eq. (3.1e) and (3.2e) and the resultant expression with eq. (3.2a) yields

$$(d\eta^\alpha)_e = +(d\eta^\epsilon)_e \qquad \text{since } z_e = -1 \tag{3.3a}$$

$$(d\eta^\alpha)_e = -z(d\eta^\alpha)_M \qquad \text{since } z \geq 1 \tag{3.3b}$$

Adding $(d\eta^\alpha)_e$ and $(d\eta^\epsilon)_{M^{z+}}$ moles to the α phase and the ϵ phase, respectively, the change in electron charges becomes [2]

$$dq^\alpha = -F(d\eta^\alpha)_e \tag{3.4a}$$

$$dq^\epsilon = +zF(d\eta^\epsilon)_{M^{z+}} \tag{3.4b}$$

Substituting eqs. (3.2a) and (3.3a) into (3.1e) and (3.1e) into (3.1d) yields

$$dU^\alpha + dU^\epsilon + zF(\phi^\alpha - \phi^\epsilon)(d\eta^\alpha)_M = 0 \tag{3.5a}$$

$$dU^\epsilon = -\left[dU^\alpha + zF(\phi^\alpha - \phi^\epsilon)(d\eta^\alpha)_M\right] \tag{3.5b}$$

Substituting eqs. (3.2a) through (3.5b) into (3.2b) and (3.2c) and the resultant expressions into (3.2a), and subsequently, collecting terms yields the entropy change of the α-ϵ system

$$dS = \left[\frac{1}{T^\alpha} - \frac{1}{T^\epsilon}\right]dU^\alpha + \left[\frac{P^\alpha}{T^\alpha} - \frac{P^\epsilon}{T^\epsilon}\right]dV^\alpha \tag{3.6}$$
$$+ \left[-\frac{(\mu^\alpha)_M}{T^\alpha} + \frac{z(\mu^\alpha)_e}{T^\alpha} - \frac{(\mu^\epsilon)_{M^{z+}}}{T^\epsilon} + \frac{(zF)(\phi^\epsilon - \phi^\alpha)}{T^\epsilon}\right](d\eta^\alpha)_M$$

At equilibrium, $dS = 0$ and the following is deduced from eq. (3.6) [2]

1) For thermal equilibrium,

$$\left[\frac{1}{T^\alpha} - \frac{1}{T^\epsilon}\right] = 0 \text{ since } T^\alpha = T^\epsilon \tag{3.7}$$

2) For mechanical equilibrium,

$$\left[\frac{P^\alpha}{T^\alpha} - \frac{P^\epsilon}{T^\epsilon}\right] = 0 \text{ since } P^\alpha = P^\epsilon \tag{3.8}$$

3) For electrochemical equilibrium, $T^\alpha = T^\epsilon$ and

$$(\mu^\alpha)_M - [z(\mu^\alpha)_e - (\mu^\epsilon)_{M^{z+}}] + zF(\phi^\alpha - \phi^\epsilon) = 0 \tag{3.9a}$$

$$(\mu^\alpha)_M - [z(\mu^\alpha)_e - (\mu^\epsilon)_{M^{z+}}] = -zF(\phi^\alpha - \phi^\epsilon) \tag{3.9b}$$

and

$$\Delta G^\alpha = (\mu^\alpha)_M - [z(\mu^\alpha)_e - (\mu^\epsilon)_{M^{z+}}] \tag{3.9c}$$

$$\Delta G^\alpha = -zF(\phi^\alpha - \phi^\epsilon) \tag{3.9d}$$

Thus, $(\mu^\alpha)_M - [z(\mu^\alpha)_e - (\mu^\epsilon)_{M^{z+}}]$ is the affinity for $M^\alpha = (M^{z+})^\epsilon + (ze^-)^\epsilon$ and ΔG^α is the Gibbs free energy change for the α-ϵ subsystem.

In addition, the potential difference $(\phi^\alpha - \phi^\epsilon)$ between two phases in a half-cell at equilibrium cannot be measured. Instead, two electrodes are connected as shown in Figure 3.1 to measure the electric potential difference between the electrodes. This can be done by connecting, say, β-δ system to the previous α-ϵ system using a salt bridge or porous membrane. Thus, the electrical potential difference between the β and α electrodes is $E = \left(\phi^\alpha - \phi^\beta\right)$. Recall that the salt bridge is a glass tube filled with an electrolyte that allows charge transfer between the cell electrolytes without disturbing the equilibrium state.

Additionally, the anodic and cathodic reactions, the Gibbs free energy changes and the electron balance expressions for the electrochemical system schematically shown in Figure 3.1 are given next.

Case 1: The electron balance in the reactions is $(z_1 e^-)^\alpha = (z_2 e^-)^\beta = ze^-$ and $\phi^\epsilon = \phi^\delta$. **Case 2:** If $(z_1 e^-)^\alpha \neq (z_2 e^-)^\beta$ and $\phi^\epsilon = \phi^\delta$, then $z = x(z_1 e^-)^\alpha = y(z_2 e^-)^\beta$, where x and y are integer numbers. Hence, the reactions are

$$M_1^\alpha = \left(M_1^{z+}\right)^\epsilon + \left(z_1 e^-\right)^\alpha \qquad \Delta G_\alpha = -zFE_\alpha \tag{3.10}$$

$$\left(M_2^{z+}\right)^\delta + \left(z_2 e^-\right)^\beta = M_2^\beta \qquad\qquad \Delta G_\beta = -zFE_\beta \tag{3.11}$$

$$M_1^\alpha + \left(M_2^{z+}\right)^\delta = \left(M_1^{z+}\right)^\epsilon + M_2^\beta \qquad \Delta G = -zFE \tag{3.12}$$

where $E_\alpha = \phi^\alpha - \phi^\epsilon$, $E_\beta = \phi^\delta - \phi^\beta$, $E = \phi^\alpha - \phi^\beta$, $\left(\mu^\beta\right)_e = (\mu^\alpha)_e$ and $\Delta G = \Delta G_\alpha + \Delta G_\beta$. In general, the standard and non-standard Gibbs free energy change expressions are, respectively

$$\Delta G^o = -zFE^o \quad \text{(standard)} \tag{3.13}$$

$$\Delta G = -zFE \quad \text{(non-standard)} \tag{3.14}$$

EX2. From thermodynamics,
The first law for a closed system is

$$dQ - dW = dU \tag{1}$$

where dV is the differential volume of the electrolyte and the total differential work due to pressure (P) and electrical potential (E) is

$$dW = dW_P + dW_e = PdV + zFdE \tag{2}$$

Combining eqs. (1) and (2) yields

$$
\begin{aligned}
dQ &= dU + dW & (3)\\
dQ &= dU + PdV + zFdE & (4)
\end{aligned}
$$

From the second law of thermodynamics,

$$
dQ = TdS \qquad (5)
$$

Then, eq. (4) becomes

$$
\begin{aligned}
TdS &= dU + PdV + zFdE & (6)\\
TdS &= dH + zFdE & (7)
\end{aligned}
$$

where dH is the differential enthalpy.

By definition, the differential Gibbs free energy is

$$
dG = dH - TdS \qquad (8)
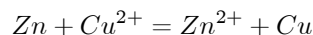$$

Combining eqs. (7) and (8) gives

$$
dG = -zFdE \qquad (9)
$$

Integrating

$$
\begin{aligned}
\Delta G^o &= -zFE^o \quad \text{(standard)} & (10)\\
\Delta G &= -zFE \quad \text{(non-standard)} & (11)
\end{aligned}
$$

EX3 3.3 *Use the data given in* Table 3.1 *to determine the half-cells and the redox standard potentials for the galvanic cell shown in* Figure 3.1 *if* $\alpha = Zn$ *and* $\beta = Cu$. *Compare the results with the data given in* Table 2.2.

Solution:
The redox reaction is

$$
Zn + Cu^{2+} = Zn^{2+} + Cu
$$

From eq. (3.16) *and Table 3.1,*

$$
\begin{aligned}
E^o_{Cu^{2+}/Cu} &= -\frac{(\nu\mu^o)_{Cu} - (\nu\mu^o)_{Cu^{2+}}}{zF}\\
E^o_{Cu^{2+}/Cu} &= -\left[\frac{(1)(0) - (1)(+64.98\ kJ/mol)}{(2)(96.50\ kJ/mol \cdot V)}\right] = +0.337\ V
\end{aligned}
$$

$$E^o_{Zn/Zn^{2+}} = -\frac{(\nu\mu^o)_{Zn^{2+}} - (\nu\mu^o)_{Zn}}{zF}$$

$$E^o_{Zn/Zn^{2+}} = -\left[\frac{(1)(-147.21\ kJ/mol) - (1)(0)}{(2)(96.50\ kJ/mol \cdot V)}\right] = +0.763\ V$$

These results are exactly the same given in Table 2.2. Thus, the standard cell potential is

$$E^o = E^o_{Cu^{2+}/Cu} + E^o_{Zn/Zn^{2+}} = +1.10\ V$$

Chapter 4

NANO ELECTROCHEMISTRY

4.1 PROBLEMS

4.1 In an electrochemical cell, the bulk electrolyte has uniform and constant ion densities, but the electrical-double layer is an inhomogeneous fluid. Why?

Answer: *The ion densities in the electrical-double layer vary in space in the vicinity of the electrode surface due to the charged particle forming the inhomogeneous structure.*

4.2 The interface region between two bulk phases may contain a complex distribution of electric charge. Name at least two causes for this phenomenon.

Answer: (a) *The charge transfer between phases and* (b) *unequal adsorption of positive and negative ions.*

4.3 Explain how it is possible for a scanning tunneling microscope (STM) to image atoms on the surface of a sample. Recall that one of the metals is the sample and the other is the probe.

Answer: *Move the tip up and down in the z-direction to obtain a constant current across the contour of the substrate (sample) surface. Then, record the position of the tip as it scans the substrate surface along the x and y directions. The tip will trace out a contour of constant probability for finding an atom on the surface. The constant tunneling current for this process can be approximated by*

$$I_t = I_o \exp\left(-\sigma z\right)$$

where I_o and σ is a constant. Nonetheless, when the tip is scanned over the surface, the tip height (z) is determined by the local geometric and electronic structure of the surface and thus it produces a surface map in real space.

4.4 For a finite depth energy well, the wave function $\psi(x)$ within the barrier of width w, the tunneling current I_t through the barrier and the decay length are related as shown below:

$$\psi(x) = \psi_o \exp(-k_2 x)$$
$$I_t \propto |\psi_o|^2 \exp(-k_2 x)$$
$$k_2 = \frac{2\pi}{h}\sqrt{2m(U_o - E)} = \frac{2\pi}{h}\sqrt{2m\chi}$$

If the work function and the barrier width are $\chi = 4.32\ eV$ and $w = 0.151$ nm in a STM experiment, then determine I_t for a barrier of width $2w$. Explain.

Solution:

$$k_2 = \left(5.1268\ nm^{-1}.eV^{-1/2}\right)(U_o - E)^{1/2}$$
$$k_2 = \left(5.1268\ nm^{-1}.eV^{-1/2}\right)\chi^{1/2} = \left(5.1268\ nm^{-1}.eV^{-1/2}\right)(4.32\ eV)^{1/2}$$
$$k_2 = 10.656\ nm^{-1}$$

Then,

$$\frac{I_{t,w}}{I_{t,2w}} = \frac{|\psi_o|^2 \exp(-k_2 w)}{|\psi_o|^2 \exp(-2k_2 w)}$$
$$\frac{I_{t,w}}{I_{t,2w}} = \exp(k_2 w) = \exp\left[\left(10.656\ nm^{-1}\right)(0.20\ nm)\right]$$
$$\frac{I_{t,w}}{I_{t,2w}} = 5 \quad \text{or} \quad I_{t,w} = 5I_{t,2w} \quad \text{or} \quad I_{t,2w} = 0.2I_{t,w}$$

Denote the significant change in $I_{t,2w}$ as $w \to 2w$. Therefore, the STM cell is very sensitive to changes in the barrier size.

4.5 Determine **(a)** the Fermi energy and **(b)** the velocity of the electron for a copper (Cu) substrate and a tungsten (W) tip in a ultra high vacuum STM cell at temperature T.

Solution:

(a) *The Fermi energy: For gold, $Cu \to Cu^{2+} + 2e^-$, with two free electron per reaction. The electron density, eq. (4.11), is*

$$\rho_{e,Cu} = [n_e \rho N_A / A_w]_{Cu}$$

$$\rho_{e,Cu} = (2)\left(\frac{8.94 \times 10^3 \ Kg/m^3}{63.55 \ Kg/Kmol}\right)\left(\frac{6.02 \times 10^{23} \ atom}{10^{-3} \ Kmol}\right)$$

$$\rho_{e,Cu} = 1.6937 \times 10^{29} \ 1/m^3$$

and

$$U_{F,Cu} = \frac{h^2}{2m_e}\left(\frac{3}{8\pi}\rho_e\right)^{2/3}$$

$$U_{F,Cu} = \frac{\left(6.63 \times 10^{-34} \ J.s\right)^2}{2*9.11 \times 10^{-31} \ Kg}\left[\left(\frac{3}{8\pi}\right)\left(7.6514 \times 10^{28} \ 1/m^3\right)\right]^{2/3}$$

$$U_{F,Cu} = 1.0541 \times 10^{-18} \ \frac{J^2.s^2}{Kg.m^2} = 1.0541 \times 10^{-18} \ J$$

$$U_{F,Cu} = \frac{1.0541 \times 10^{-18} \ J}{1.60 \times 10^{-19} \ J/eV} = 6.59 \ eV$$

The units: $J^2.s^2/\left(Kg.m^2\right) = J^2/\left(N.m\right) = J$. Similarly, for tungsten, $W \rightarrow W^{4+} + 4e^-$, with 4 free electrons, eqs. (4.7) and (4.6) give

$$\rho_{e,W} = [n_e \rho N_A / A_w]_W$$

$$\rho_{e,W} = (4)\left(\frac{19.3 \times 10^3}{183.85}\right)\left(\frac{6.02 \times 10^{23}}{10^{-3}}\right) = 2.5278 \times 10^{29} \ 1/m^{-3}$$

$$U_{F,W} = \frac{\left(6.63 \times 10^{-34} \ J.s\right)^2}{2*9.11 \times 10^{-31} \ Kg}\left(\frac{3*1.694 \times 10^{29}}{8\pi}\frac{1}{m^3}\right)^{2/3} = 2.3383 \times 10^{-18} \ J$$

$$U_{F,W} = \frac{2.3383 \times 10^{-18} \ J}{1.60 \times 10^{-19} \ J/eV} = 14.61 \ eV$$

Obviously, $U_{F,W} > U_{F,Cu}$ due to the differences in the amount of free electrons and the electron densities between gold and tungsten metals.

(b) The velocity of electrons: Using eq. (4.12) yields

$$v_e = \sqrt{\frac{2U_F}{m_e}}$$

$$v_{e,Cu} = \sqrt{\frac{2\left(1.0541 \times 10^{-18} \ J\right)}{9.11 \times 10^{-31} Kg}} = 1.52 \times 10^6 \sqrt{\frac{N.m}{Kg}}$$

$$v_{e,Cu} = 1.52 \times 10^6 \sqrt{\frac{Kg.m}{s^2}\frac{m}{Kg}} = 1.52 \times 10^6 \ m/s$$

and for tungsten

$$v_{e,W} = \sqrt{\frac{(2)\,(2.3383 \times 10^{-18}\ J)}{9.11 \times 10^{-31} Kg}}$$

$$v_{e,W} = 2.27 \times 10^6\ m/s = 2,270\ Km/s$$

Therefore, an electron travels very fast in the vacuum gap. Let's determine the atom density using eq. (4.9)

$$n_{a,Cu} = \frac{\rho N_A}{A_w} = \frac{(8.94 \times 10^3\ Kg/m^3)}{63.55\ Kg/Kmol}\left(\frac{6.02 \times 10^{23}\ atoms}{10^{-3}\ Kmol}\right)$$

$$n_{a,Cu} = 8.4687 \times 10^{28}\ atoms/m^3$$

$$n_{a,W} = \frac{\rho N_A}{A_w} = \frac{(19.30 * 10^3\ Kg/m^3)}{183.85\ Kg/Kmol}\left(\frac{6.02 * 10^{23}\ atoms}{10^{-3}\ Kmol}\right)$$

$$n_{a,W} = 6.3196 \times 10^{28}\ atoms/m^3$$

Verify the number of free electrons being used. Thus,

$$n_{e,Cu} = \left(\frac{\rho_e}{n_a}\right)_{Cu} = \frac{1.6937 \times 10^{29}\ 1/m^3}{1.8302 \times 10^{29}\ atoms/m^3} = 2$$

$$n_{e,W} = \left(\frac{\rho_e}{n_a}\right)_{W} = \frac{2.5278 \times 10^{29}}{6.3196 \times 10^{28}} = 4$$

According to the above calculations, the amount of energy (offset) being given to the electrons during tunneling is

$$\chi = E_{F,Cu}^S - E_{F,W}^T = 6.59\ eV - 14.61\ eV = -8.02\ eV$$

This is the energy that causes the electrons to acquire a specific velocity in the tunneling gap (electrical conduction region).

4.6 For the reaction $O + e^- \rightleftarrows R$ in an electrochemical cell, the cyclic voltammetry method provided the formal potential (standard potential) $\phi^o = 133\ mV$ against a reference electrode. If the activity ratio is $[O]/[R] = 0.2$, then calculate (a) the applied potential ϕ at 25^oC and (b) the required energy for the reaction to proceed to the right as written.

Solutions:
(a) *Using the Nernst equation yields*

$$\phi = \phi^o - \frac{RT}{zF} \ln \frac{[R]}{[O]}$$

$$\phi = \phi^o + \frac{RT}{zF} \ln \frac{[O]}{[R]} = 0.133 \ V + \frac{(8.314 \ J/mol.K)(298 \ K)}{(1)(96,500 \ J/mol.V)} \ln (0.2)$$

$$\phi = 0.09168 \ V = 91.68 \ mV$$

(b) *The reaction energy:*

$$U = q_e\phi = \left(1.602 \times 10^{-19} \ J/V\right)(0.09168 \ V) = 1.4687 \times 10^{-20} \ J$$

$$U = 0.092 \ eV$$

4.7 Show that $P_T = \exp(-2k_2x)$, eq. (4.48), using the following equations

$$\psi = A \exp(i\theta)$$

$$\frac{d^2\psi}{dx^2} = -\frac{\sqrt{2m[U-E]}}{\hbar^2}\psi = -\frac{P^2}{\hbar^2}\psi$$

where P is the moment, $x = w$ and $\hbar = h/2\pi$. Hint: extract the resultant real and imaginary parts for solving this problem.

Solution:

Derivatives:

$$\psi = A \exp(i\theta) \tag{a}$$

$$\frac{d\psi}{dx} = \left[\frac{dA}{dx} + iA\frac{d\theta}{dx}\right]\exp(i\theta)$$

$$\frac{d^2\psi}{dx^2} = \left[\frac{d^2A}{dx^2} + iA\frac{d^2\theta}{dx^2} + 2i\frac{dA}{dx}\frac{d\theta}{dx} - A\left(\frac{d\theta}{dx}\right)^2\right]\exp(i\theta) \tag{b}$$

$$\frac{d^2\psi}{dx^2} = \left[\frac{d^2A}{dx^2} + iA\frac{d^2\theta}{dx^2} + 2i\frac{dA}{dx}\frac{d\theta}{dx} - A\left(\frac{d\theta}{dx}\right)^2\right]\frac{\psi}{A}$$

Equate $d^2\psi/dx^2$ terms:

$$-\frac{P^2}{\hbar^2}\psi = \left[\frac{d^2A}{dx^2} + iA\frac{d^2\theta}{dx^2} + 2i\frac{dA}{dx}\frac{d\theta}{dx} - A\left(\frac{d\theta}{dx}\right)^2\right]\frac{\psi}{A}$$

$$-\frac{AP^2}{\hbar^2} = \left[\frac{d^2A}{dx^2} + iA\frac{d^2\theta}{dx^2} + 2i\frac{dA}{dx}\frac{d\theta}{dx} - A\left(\frac{d\theta}{dx}\right)^2\right] \tag{c}$$

Imaginary parts:of eq. (c) and multiply by A and eliminate i:

$$0 = iA\frac{d^2\theta}{dx^2} + 2i\frac{dA}{dx}\frac{d\theta}{dx}$$

$$0 = A^2\frac{d^2\theta}{dx^2} + 2A\frac{dA}{dx}\frac{d\theta}{dx} \tag{d}$$

Eq. (d) becomes

$$\left[A^2\frac{d^2\theta}{dx^2}\right]/dx = 0 \tag{e}$$

Integrating eq. (e) yields the wave amplitude A as

$$A^2\frac{d\theta}{dx} = C_1$$

$$A = \frac{\sqrt{C_1}}{\sqrt{d\theta/dx}} = \frac{C}{\sqrt{d\theta/dx}} \tag{f}$$

Real Parts of eq. (c):

$$-\frac{AP^2}{\hbar^2} = \frac{d^2A}{dx^2} - A\left(\frac{d\theta}{dx}\right)^2$$

$$-\frac{P^2}{\hbar^2} = \frac{1}{A}\frac{d^2A}{dx^2} - \left(\frac{d\theta}{dx}\right)^2$$

and

$$\frac{1}{A}\frac{d^2A}{dx^2} = \left(\frac{d\theta}{dx}\right)^2 - \frac{P^2}{\hbar^2}$$

If

$$\frac{1}{A}\frac{d^2A}{dx^2} < < \left(\frac{d\theta}{dx}\right)^2 - \frac{P^2}{\hbar^2}$$

$$\left[\frac{1}{A}\frac{d^2A}{dx^2}\right] \rightarrow 0$$

then

$$\left(\frac{d\theta}{dx}\right)^2 = \frac{P^2}{\hbar^2}$$

$$\frac{d\theta}{dx} = \frac{P}{\hbar}$$

$$\theta = \frac{1}{\hbar}\int P dx \tag{g}$$

and

$$A = \frac{\sqrt{C_1}}{\sqrt{d\theta/dx}} = \frac{C}{\sqrt{d\theta/dx}} = \frac{\hbar C}{\sqrt{P}}$$

$$A = \frac{D}{\sqrt{P}}$$

Thus,

$$\psi = A \exp(i\theta)$$

$$\psi = \frac{D}{\sqrt{P}} \exp\left[\frac{i}{\hbar} \int P dx\right] \qquad \text{(h)}$$

But,

$$P = \sqrt{2m(E-U)}$$

$$P = i\sqrt{2m(U-E)}$$

and eq. (h) along with $i^2 = \left(\sqrt{-1}\right)^2 = -1$ *and fixed* $U = U_o$

$$\psi = \frac{D}{\sqrt{P}} \exp\left[\frac{i^2}{\hbar} \int \sqrt{2m(U-E)} dx\right]$$

$$\psi = \frac{D}{\sqrt{P}} \exp\left[-\int \frac{\sqrt{2m(U-E)}}{\hbar} dx\right]$$

$$\psi = \frac{D}{\sqrt{P}} \exp\left[-\frac{2\pi}{h} \sqrt{2m[U(x)-E]} \int dx\right]$$

$$\psi = \frac{D}{\sqrt{P}} \exp\left[-\int k_2 dx\right]$$

$$\psi = \frac{D}{\sqrt{P}} \exp\left[-\int_0^x k_2 dx\right] = \frac{D}{\sqrt{P}} \exp(-k_2 x)$$

$$\frac{\psi\sqrt{P}}{D} = \exp(-k_2 x)$$

where

$$k_2 = \frac{2\pi}{h} \sqrt{2m[U(x)-E]}$$

Then,

$$P_T = \left(\frac{\psi\sqrt{P}}{D}\right)^2$$

$$P_T = \exp(-2k_2 x)$$

where x is the barrier width and according to Figure 4.10, $x = x_2 - x_1 = w$

4.8 Below is a sketch for the principle of the STM technique. If the work function (χ) and the tunneling gap column (z) are $4\ eV$ and $0.3\ nm$, respectively, calculate the probability for an electron to tunnel from the probe tip to the metal sample.
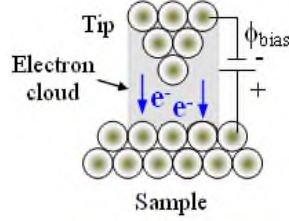
Solution:

$$k_2 = \left(5.1268\ nm^{-1}.eV^{-1/2}\right)(U_o - E)^{1/2} = \left(5.1268\ nm^{-1}.eV^{-1/2}\right)(4\ eV)^{1/2}$$
$$k_2 = 10.254 nm^{-1}$$

and

$$P_T = \exp\left(-2k_2 z\right) = \exp\left[-2\left(10.254\ nm^{-1}\right)(0.3\ nm)\right] = 2.13 \times 10^{-3}$$
$$P_T \simeq 0.21\%$$

4.9 Calculate the electron energy (E) if the tunneling probability (P_T) is 0.106 and the barrier height (U_o) 4.5 eV. Assume a barrier width of 0.4 nm.

Solution:

$$P_T = \exp\left(-2k_2 w\right)$$
$$k_2 = -\ln\left(P_T\right)/2w = -\ln\left(0.106\right)/(2x0.4) = 2.81\ nm^{-1}$$

Then,

$$k_2 = \left(5.1268\ nm^{-1}.eV^{-1/2}\right)(U_o - E)^{1/2}$$
$$E = U_o - (2.81/5.1268)^2 = 4.5\ eV - (2.81/5.1268)^2\ eV$$
$$E = 4.2\ eV$$

4.10 Assuming that there is no wave reflection, eq. (4.20), at the boundary $x = 0$, derive $P_R = |B/A|^2$ and P_T for $E > U_o$. Use the continuity of the wave function and its derivative at the origin.

Solution:
From eq. (4.20),

$$\begin{aligned}
\psi_1(x) &= A \exp(ik_1 x) + B \exp(-ik_1 x) \\
\frac{d\psi_1(x)}{dx} &= ik_1 A \exp(ik_1 x) - ik_1 B \exp(-ik_1 x)
\end{aligned}$$

$$\begin{aligned}
\psi_2(x) &= C \exp(ik_2 x) + D \exp(-ik_2 x) \\
\psi_2(x) &= C \exp(ik_2 x) \quad \text{since } D = 0 \\
\frac{d\psi_2(x)}{dx} &= ik_2 C \exp(ik_2 x) - ik_2 D \exp(-ik_2 x) \\
\frac{d\psi_2(x)}{dx} &= ik_2 C \exp(ik_2 x) \quad \text{since } D = 0
\end{aligned}$$

At $x = 0$,

$$\begin{aligned}
\psi(0)_1 &= \psi(0)_2 \\
A + B &= C \qquad\qquad (1) \\
\frac{d\psi_1(0)}{dx} &= \frac{d\psi_2(0)}{dx} \\
A - B &= \frac{ik_2}{ik_1} C \qquad\qquad (2)
\end{aligned}$$

or

$$\begin{aligned}
1 + \frac{B}{A} &= \frac{C}{A} \\
1 + \frac{B}{A} &= \frac{k_2}{k_1}\frac{C}{A}
\end{aligned}$$

Combining eqs. (1) *and* (2) *gives*

$$\begin{aligned}
1 + \frac{B}{A} &= \frac{k_2}{k_1}\left(1 + \frac{B}{A}\right) = \frac{k_2}{k_1} + \frac{k_2}{k_1}\frac{B}{A} \\
\left(1 - \frac{k_2}{k_1}\right)\frac{B}{A} &= 1 + \frac{k_2}{k_1} \\
\frac{B}{A} &= \frac{1 + k_2/k_1}{1 - k_2/k_1}
\end{aligned}$$

Then,

$$P_R = \left|\frac{B}{A}\right|^2 = \left|\frac{1 + k_2/k_1}{1 - k_2/k_1}\right|^2$$

and

$$
\begin{aligned}
P_T + P_R &= 1 \\
P_T &= 1 - P_R \\
P_T &= 1 - \left|\frac{1 + k_2/k_1}{1 - k_2/k_1}\right|^2
\end{aligned}
$$

4.11   Assuming that the wave amplitude, eq. (4.23), $C = 0$ when $x \to \infty$, derive $P_R = |B/A|^2$ and P_T for $E < U_o$. Use the continuity of the wave function and its derivative at the origin. Explain.

Solution:

From eq. (4.31) through) (4.34),

$$
\begin{aligned}
A + B &= C + D & (4.31) \\
ik_1 (A + B) &= k_2 (C + D) & (4.32) \\
C \exp(k_2 w) + D \exp(-k_2 w) &= F \exp(ik_1 w) & (4.33) \\
k_2 [C \exp(k_2 w) - D \exp(-k_2 w)] &= ik_1 F \exp(ik_1 w) & (4.34)
\end{aligned}
$$

Divide these eqs. by A so that

$$
\begin{aligned}
A + B &= C + D & \text{(a)} \\
ik_1 (A + B) &= k_2 (C + D) & \text{(b)} \\
C \exp(k_2 w) + D \exp(-k_2 w) &= F \exp(ik_1 w) & \text{(c)} \\
k_2 [C \exp(k_2 w) - D \exp(-k_2 w)] &= ik_1 F \exp(ik_1 w) & \text{(d)}
\end{aligned}
$$

and

$$
\begin{aligned}
\psi_1(x) &= A \exp(ik_1 x) + B \exp(-ik_1 x) \\
\frac{d\psi_1(x)}{dx} &= ik_1 A \exp(ik_1 x) - ik_1 B \exp(-ik_1 x)
\end{aligned}
$$

$$
\begin{aligned}
\psi_2(x) &= C \exp(ik_2 x) + D \exp(-ik_2 x) \\
\psi_2(x) &= D \exp(-ik_2 x) \quad \text{since } C = 0 \\
\frac{d\psi_2(x)}{dx} &= -ik_2 D \exp(-ik_2 x)
\end{aligned}
$$

At $x = 0$,

$$
\begin{aligned}
\psi\left(0\right)_1 &= \psi\left(0\right)_2 \\
A + B &= D \quad (1) \\
\frac{d\psi_1\left(0\right)}{dx} &= \frac{d\psi_2\left(0\right)}{dx} \\
A - B &= -\frac{ik_2}{ik_1}D \quad (2)
\end{aligned}
$$

Divide eqs. (1) and (2) by A so that

$$
\begin{aligned}
1 + \frac{B}{A} &= \frac{D}{A} \quad (3) \\
1 - \frac{B}{A} &= -\frac{k_2}{k_1}\frac{D}{A} \quad (4)
\end{aligned}
$$

Eliminate D/A

$$
\begin{aligned}
1 + \frac{B}{A} &= -\frac{k_2}{k_1}\left(1 + \frac{B}{A}\right) = -\frac{ik_2}{ik_1} - \frac{k_2}{k_1}\frac{B}{A} \\
\frac{B}{A}\left(1 + \frac{k_2}{k_1}\right) &= -\frac{k_2}{k_1} - 1 \\
\frac{B}{A} &= -\frac{1 + k_2/k_1}{1 + k_2/k_1}
\end{aligned}
$$

Then,

$$
\begin{aligned}
P_R &= \left|\frac{B}{A}\right|^2 = \left|-\frac{1 + k_2/k_1}{1 + k_2/k_1}\right|^2 = 1 \\
P_T + P_R &= 1 \\
P_T &= 1 - 1 = 0
\end{aligned}
$$

The particle will always be reflected at $x = 0$. This means that the particle can not penetrate into the classically forbidden barrier (region 2, Figure 4.10) and therefore, there is no particle transmission.

4.12 For $E < U_o$, use eq. (4.23) to show that

$$
\begin{aligned}
\frac{F}{A} &= \frac{4ik_1k_2\exp\left(-ik_1w\right)}{\left(k_2 + ik_1\right)^2\exp\left(-k_2w\right) - \left(k_2 - ik_1\right)^2\exp\left(k_2w\right)} \\
P_T &= \frac{16k_1^2k_2^2}{\left[\left(k_1 + k_2\right)^2 e^{-2k_2w} + \left(k_1 + k_2\right)^2 e^{2k_2w}\right] + \left[12k_1^2k_2^2 - 2\left(k_2^4 + k_1^4\right)\right]}
\end{aligned}
$$

Solution:

$$\psi\left(w\right)_2 = \psi\left(w\right)_3$$

$$C\exp\left(k_2 w\right) + D\exp\left(-k_2 w\right) = F\exp\left(k_1 w\right) \tag{3}$$

$$\frac{d\psi_2\left(w\right)}{dx} = \frac{d\psi_3\left(w\right)}{dx}$$

$$k_2 C\exp\left(k_2 w\right) - k_2 D\exp\left(-k_2 w\right) = ik_1 F\exp\left(ik_1 w\right) \tag{4}$$

Divide eqs. (a) *through* (d) *by* A *and group them to be algebraically manipulated.*

$$A + B = C + D \tag{5}$$

$$A - B = \frac{k_2}{ik_1}C - \frac{k_2}{ik_1}D \tag{6}$$

$$C\exp\left(k_2 w\right) + D\exp\left(-k_2 w\right) = F\exp\left(k_1 w\right) \tag{7}$$

$$C\exp\left(k_2 w\right) - D\exp\left(-k_2 w\right) = \frac{ik_1}{k_2}F\exp\left(ik_1 w\right) \tag{8}$$

The tedious work: Divide by A

$$1 + \frac{B}{A} = \frac{C}{A} + \frac{D}{A} \tag{9}$$

$$\frac{ik_1}{k_2} - \frac{ik_1}{k_2}\frac{B}{A} = \frac{C}{A} - \frac{D}{A} \tag{10}$$

$$\frac{C}{A}\exp\left(k_2 w\right) + \frac{D}{A}\exp\left(-k_2 w\right) = \frac{F}{A}\exp\left(k_1 w\right) \tag{11}$$

$$\frac{C}{A}\exp\left(k_2 w\right) - \frac{D}{A}\exp\left(-k_2 w\right) = \frac{ik_1}{k_2}\frac{F}{A}\exp\left(ik_1 w\right) \tag{12}$$

Add eqs. (11) *and* (12) *to get*

$$2\frac{C}{A}\exp\left(k_2 w\right) = \left(\frac{ik_1}{k_2} + 1\right)\frac{F}{A}\exp\left(ik_1 w\right)$$

$$\frac{C}{A} = \frac{F}{A}\left(\frac{k_2 + ik_1}{2k_2}\right)\exp\left(ik_1 w\right)\exp\left(-k_2 w\right) \tag{13}$$

Next, subtract eqs. (11) $-$ (12)

$$2\frac{D}{A}\exp\left(-k_2 w\right) = \left(1 - \frac{ik_1}{k_2}\right)\frac{F}{A}\exp\left(ik_1 w\right)$$

$$\frac{D}{A} = \frac{F}{A}\left(\frac{k_2 - ik_1}{2k_2}\right)\exp\left(ik_1 w\right)\exp\left(k_2 w\right) \tag{14}$$

Add eqs. (10) + (9) to get

$$2\frac{C}{A} = \frac{ik_1}{k_2} - \frac{ik_1}{k_2}\frac{B}{A} + 1 + \frac{B}{A}$$

$$\frac{C}{A} = \frac{k_2 + ik_1}{2k_2} + \left(\frac{k_2 - ik_1}{2k_2}\right)\frac{B}{A} \qquad (15)$$

Subtract eqs. (9) − (10) so that

$$2\frac{D}{A} = \left(1 - \frac{ik_1}{k_2}\right) + \left(1 + \frac{ik_1}{k_2}\right)$$

$$\frac{D}{A} = \frac{k_2 - ik_1}{2k_2} + \left(\frac{k_2 + ik_1}{2k_2}\right)\frac{B}{A} \qquad (16)$$

Now, equate eqs. (13) = (15)

$$\frac{F}{A}\left(\frac{k_2 + ik_1}{2k_2}\right)\exp\left(ik_1w\right)\exp\left(-k_2w\right) = \frac{k_2 + ik_1}{2k_2} + \left(\frac{k_2 - ik_1}{2k_2}\right)\frac{B}{A}$$

$$\frac{F}{A}\left(k_2 + ik_1\right)\exp\left(ik_1w\right)\exp\left(-k_2w\right) = \left(k_2 + ik_1\right) + \left(k_2 - ik_1\right)\frac{B}{A} \qquad (17)$$

Equate eqs. (14) = (16)

$$\frac{F}{A}\left(\frac{k_2 - ik_1}{2k_2}\right)\exp\left(ik_1w\right)\exp\left(k_2w\right) = \frac{k_2 - ik_1}{2k_2} + \left(\frac{k_2 + ik_1}{2k_2}\right)\frac{B}{A}$$

$$\frac{F}{A}\left(k_2 - ik_1\right)\exp\left(ik_1w\right)\exp\left(k_2w\right) = \left(k_2 - ik_1\right) + \left(k_2 + ik_1\right)\frac{B}{A} \qquad (18)$$

Rearrange eqs. (17) and (18) so that

$$\frac{F}{A}\left(k_2 + ik_1\right)\exp\left(ik_1w\right)\exp\left(-k_2w\right) - \left(k_2 + ik_1\right) = \left(k_2 - ik_1\right)\frac{B}{A} \qquad (19)$$

$$\frac{F}{A}\left(k_2 + ik_1\right)\exp\left(ik_1w\right)\exp\left(-k_2w\right) - \left(k_2 - ik_1\right) = \left(k_2 + ik_1\right)\frac{B}{A} \qquad (20)$$

Now divide eqs. (19)/(20) to eliminate B/A

$$\frac{\frac{F}{A}\left(k_2 + ik_1\right)\exp\left(ik_1w\right)\exp\left(-k_2w\right) - \left(k_2 + ik_1\right)}{\frac{F}{A}\left(k_2 + ik_1\right)\exp\left(ik_1w\right)\exp\left(-k_2w\right) - \left(k_2 - ik_1\right)} = \frac{k_2 - ik_1}{k_2 + ik_1} \qquad (21)$$

Solve for F/A

$$P_T \quad = \quad \left| \frac{F}{A} \right|^2 = \frac{F^*F}{A^*A}$$

$$\frac{F}{A} \quad = \quad \frac{4k_1k_2e^{ik_1w}}{(k_2+ik_1)^2\,e^{-k_2w}-(k_2-ik_1)^2\,e^{k_2w}}$$

$$\frac{F^*}{A^*} \quad = \quad \frac{-4k_1k_2e^{-ik_1w}}{(k_2-ik_1)^2\,e^{-k_2w}-(k_2+ik_1)^2\,e^{k_2w}} \quad (Conjugate)$$

$$\frac{F^*F}{A^*A} \quad = \quad \frac{-4k_1k_2e^{-ik_1w}}{\left[(k_2-ik_1)^2\,e^{-k_2w}-(k_2+ik_1)^2\,e^{k_2w}\right]}$$

$$x\frac{4k_1k_2e^{ik_1w}}{\left[(k_2+ik_1)^2\,e^{-k_2w}-(k_2-ik_1)^2\,e^{k_2w}\right]}$$

Algebiaic work for the denominator:

$$[(k_2-ik_1)(k_2+ik_1)]^2\,e^{-k_2w}e^{-k_2w} = \left(k_1^2+k_2^2\right)^2\,e^{-2k_2w}$$

$$-[(k_2-ik_1)(k_2-ik_1)]^2\,e^{-k_2w}e^{k_2w} = 4ik_1k_2^3-k_2^4-k_1^4-4ik_1^3k_2+6k_1^2k_2^2$$

$$-(k_2+ik_1)^2(k_2+ik_1)^{22}\,e^{k_2w2}e^{-k_2w} = 4ik_1^3k_2-k_2^4-4ik_1k_2^3-k_1^4+6k_1^2k_2^2$$

$$[(k_2+ik_1)(k_2-ik_1)]^2 = \left(k_1^2+k_2^2\right)^2\,e^{2k_2w}$$

$$X \quad = \quad 4ik_1k_2^3-k_2^4-k_1^4-4ik_1^3k_2+6k_1^2k_2^2+4ik_1^3k_2-k_2^4-4ik_1k_2^3-k_1^4+6k_1^2k_2^2$$
$$Y \quad = \quad 12k_1^2k_2^2-2k_2^4-2k_1^4$$
$$X \quad = \quad Y$$

Then, the full-blown tunneling probability equation becomes

$$P_T \quad = \quad \left| \frac{F}{A} \right|^2 = \frac{F^*F}{A^*A}$$

$$P_T \quad = \quad \frac{16k_1^2k_2^2}{(k_1+k_2)^2\,e^{-2k_2w}+(k_1+k_2)^2\,e^{2k_2w}+12k_1^2k_2^2-2k_2^4-2k_1^4}$$

$$P_T \quad = \quad \frac{16k_1^2k_2^2}{\left[(k_1+k_2)^2\,e^{-2k_2w}+(k_1+k_2)^2\,e^{2k_2w}\right]+[12k_1^2k_2^2-2\left(k_2^4+k_1^4\right)]}$$

Test:
If $k_1 = 14$, $k_2 = 7$ and $w = 1.2$, then

$$P_T = \frac{16k_1^2 k_2^2}{(k_1 + k_2)^2 e^{-2k_2 w} + (k_1 + k_2)^2 e^{2k_2 w} + 12k_1^2 k_2^2 - 2(k_2^4 + k_1^4)}$$

$$P_T = 1.7619 \times 10^{-5}$$

$$(k_1 + k_2)^2 e^{-2k_2 w} + (k_1 + k_2)^2 e^{2k_2 w} = 8.7214 \times 10^9$$
$$12k_1^2 k_2^2 - 2(k_2^4 + k_1^4) = 33,614$$

$$\left[(k_1 + k_2)^2 e^{-2k_2 w} + (k_1 + k_2)^2 e^{2k_2 w} \right] > > \left[12k_1^2 k_2^2 - 2(k_2^4 + k_1^4) \right]$$
$$8.7214 \times 10^9 > > 33,614$$

According to these results, the full-blown equation can be simplified as

$$P_T = \frac{16k_1^2 k_2^2}{(k_1 + k_2)^2 e^{-2k_2 w} + (k_1 + k_2)^2 e^{2k_2 w}} = 1.7619 \times 10^{-5}$$

If $e^{2k_2 w} >> e^{-2k_2 w}$, then a further simplification of the P_T equations ontained as

$$P_T = \frac{16k_1^2 k_2^2}{(k_1 + k_2) e^{2k_2 w}} = 1.7619 \times 10^{-5}$$

Thus,

$$P_T = \left| \frac{F}{A} \right|^2 = \frac{F^* F}{A^* A} = \frac{16k_1^2 k_2^2}{(k_2^2 - k_1^2)^2} \exp(-k_2 w)$$

Chapter 5

KINETICS OF ACTIVATION POLARIZATION

5.1 PROBLEMS/QUESTIONS

5.1 What are the three conditions for galvanic corrosion to occur?

Answer: *Dissimilar metals, corrosive media, and electrical contact.*

5.2 If the state of equilibrium of an electrochemical cell is disturbed by an applied current density i_x, then $i_a = -i_c = i_{corr}$ no longer holds. Let i_x be a cathodic current density and the slope of the corresponding polarization curve be $dE/d\log(i_x)$, which increases approaching the Tafel constant β_c. Determine a) the value of i_x when $i_c = 10^{-3}$ A/cm^2 and $i_a = 10^{-9}$ A/cm^2 and b) the value of β_c when $i_{corr} = 10^{-5}$ A/cm^2 and $\eta = -0.20$ V.

Solution:

a) $i_x = i_c - i_a \approx i_c = 10^{-3}$ A/cm^2
b) *The cathodic overpotential is given by*

$$
\begin{aligned}
\eta_c &= -\beta_c \log \frac{i_x}{i_{corr}} \\
\beta_c &= -\frac{\eta_c}{\log(i_x/i_{corr})} = \frac{0.20}{\log(10^{-3}/10^5)} \\
\beta_c &= 0.10 \ V
\end{aligned}
$$

5.3 According to the Stockholm Convention Cell $Fe\,|Fe^{+2}|\,|H^+, H_2|\,Pt$, the corrosion potential of iron (Fe) is -0.70 V_{SCE} at $pH = 4.4$ and 25^oC in a

41

deaerated (no oxygen is involved) acid solution. Calculate a) the corrosion rate in mm/y when

$$i_{o,H} = 10^{-6} \ A/cm^2 \qquad \beta_c = -0.10 \ V_{SHE}$$
$$i_{o,Fe} = 10^{-8} \ A/cm^2 \qquad E_{Fe} = -0.50 \ V_{SHE}$$

b) the Tafel anodic slope β_a and c) draw the kinetic diagram E $vs.$ $\log i$.

Solutions:

$$
\begin{array}{lll}
Fe \rightarrow Fe^{+2} + 2e & \Rightarrow & E_{Fe} = -0.50 \ V \\
The\ possible\ reactions\ are \quad 2H^+ + 2e \rightarrow H_2 & \Rightarrow & E_H =? \\
\hline
Fe + 2H^+ \rightarrow Fe^{+2} + H_2 & \Rightarrow & E = E_{Fe} + E_H
\end{array}
$$

a) $From$ Table 2.7 and $Nernst$ $equation,$

$$
\begin{aligned}
E_{corr} &= -0.70 + 0.241 \approx -0.46 \ V_{SHE} \\
E_H &= E_H^o - \frac{RT}{zF} \ln \frac{[H_2]}{[H^+]^2} = E_H^o + \frac{4.606RT}{zF} \log \left[H^+ \right] \\
E_H &= E_H^o - \frac{4.606RT}{zF} (pH) \\
E_H &= 0 - \frac{(4.606)(8.314 \ J/mol.K)(298K)}{(2)(96,500 \ J/mol.V)} (pH) \\
E_H &= -(0.0591)(4.4) = -0.26 \ V
\end{aligned}
$$

$Thus,$ the $cell$ $potential$ and the $overpotentials$ $becomes$

$$
\begin{aligned}
E &= E_{Fe} + E_H = -0.50 \ V - 0.26 \ V = -0.76 \ V \\
\eta_a &= E_{Fe} - E_{corr} = -0.46 \ V + 0.50 \ V = -0.04 \ V \\
\eta_c &= E_H - E_{corr} = -0.26 \ V + 0.46 \ V = -0.20 \ V
\end{aligned}
$$

$Using$ eq. (5.35) $yields$ the $corrosion$ $current$ $density$

$$
\begin{aligned}
\eta_c &= -\beta_c \log \left(\frac{i_{o,H}}{i_{corr}} \right) \\
i_{corr} &= i_{o,H} 10^{\eta_c/\beta_c} \\
i_{corr} &= \left(10^{-6} \ A/cm^2 \right) 10^{0.2/0.10} \\
i_{corr} &= \left(10^{-6} \ A/cm^2 \right) 10^2 \\
i_{corr} &= 10^{-4} \ A/cm^2
\end{aligned}
$$

$Using$ eq. (5.48) $gives$ the $iron$ $corrosion$ $rate$

$$
\begin{aligned}
C_R &= \frac{i_{corr} A_w}{zF\rho} = \frac{\left(10^{-4} \ A/cm^2 \right)(55.85 \ g/mol)}{(2)(96,500 \ A.s/mol)(7.86 \ g/cm^3)} \\
C_R &= 3.68x10^{-9} \ cm/s = 1.16 \ mm/y
\end{aligned}
$$

b) *From* eq. (5.32),

$$\eta_a = \beta_a \log\left(\frac{i_{corr}}{i_{o,Fe}}\right)$$

$$\beta_a = \eta_a / \log\left(\frac{i_{corr}}{i_{o,Fe}}\right)$$

$$\beta_a = (0.04\ V) / \log\left(10^{-4} A/cm^2 / 10^{-8} A/cm^2\right)$$

$$\beta_a = 0.01\ V$$

c) *The required diagram is*
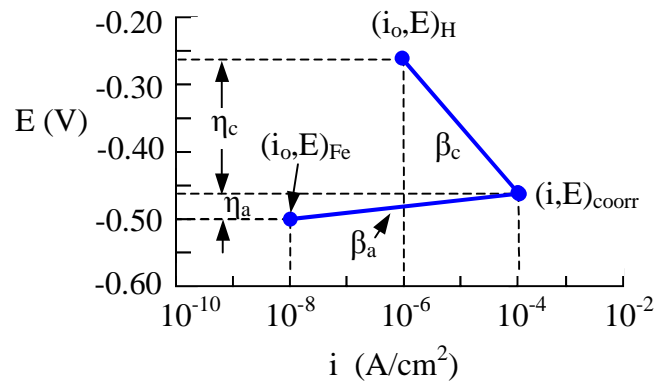
5.4 Let the following anodic and cathodic reactions be, respectively

$$M = M^{+2} + 2e^- \qquad E_M = -0.941\ V_{SCE} \qquad i_{o,M} = 10^{-2}\ \mu A/cm^2$$
$$2H^+ + 2e^- = H_2 \qquad E_H = -0.200\ V_{SHE} \qquad i_{o,H} = 0.10\ \mu A/cm^2$$
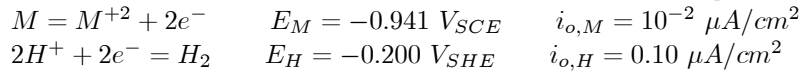
where $i_{corr} = 10^2\ \mu A/cm^2$ and $E_{corr} = -0.741\ V_{SCE}$. a) Construct the corresponding kinetic diagram and b) determine both β_a and β_c from the diagram and from the definition of overpotential equations.

Solutions:

From Table 2.7,

$$E_M = -0.941 + 0.241 = -0.70\ V$$
$$E_{corr} = -0.741 + 0.241 = -0.50\ V$$

Thus, the required diagram is
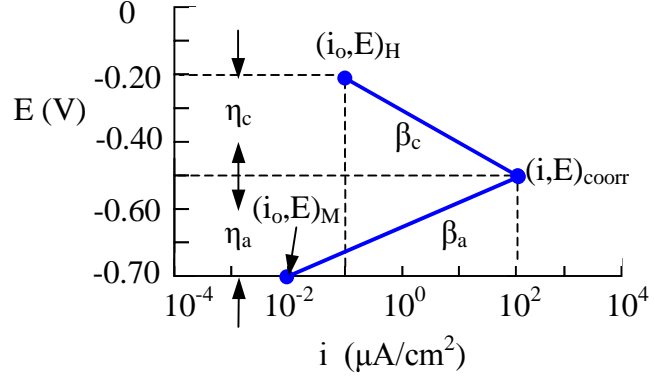
From the diagram,

$$
\begin{aligned}
\beta_a &= \frac{E_{corr} - E_M}{4 \ decades} = \frac{(-0.50 \ V) - (-0.70 \ V)}{4} \\
\beta_a &= 0.05 \ V \\
\beta_c &= \frac{E_{corr} - E_H}{3 \ decades} = \frac{(-0.20 \ V) - (-0.50 \ V)}{3} \\
\beta_c &= 0.10 \ V
\end{aligned}
$$

From the overpotential eq. (5.32),

$$
\begin{aligned}
\eta_a &= E_{corr} - E_M = 0.20 \ V \\
\eta_c &= E_{corr} - E_H = -0.30 \ V \\
\eta_a &= \beta_a \log\left(\frac{i_{corr}}{i_{o,M}}\right) \\
\eta_c &= -\beta_c \log\left(\frac{i_{corr}}{i_{o,H}}\right)
\end{aligned}
$$

Then,

$$
\begin{aligned}
\beta_a &= \eta_a / \log\left(\frac{i_{corr}}{i_{o,M}}\right) \\
\beta_a &= (0.20 \ V) / \log\left[\left(10^2 \mu A/cm^2\right)/10^{-2} \mu A/cm^2\right] \\
\beta_a &= 0.05 \ V
\end{aligned}
$$

and

$$\beta_c = -\eta_c / \log\left(\frac{i_{corr}}{i_{o,H}}\right)$$

$$\beta_c = (-0.30 \ V)\,/\log\left[\left(10^2 \mu A/cm^2\right)/\left(0.10 \mu A/cm^2\right)\right]$$

$$\beta_c = 0.10 \ V$$

5.5 A steel tank is hot dipped in a deaerated acid solution of $5x10^{-4}$ mol/cm^3 molality zinc chloride $(ZnCl_2)$ so that a 0.15-mm zinc coating is deposited on the steel surface. This process produces a galvanized steel tank. Calculate the time it takes for the zinc coating to corrode completely at a $pH = 4$. Data: $E_{Zn} = -0.8 \ V$, $i_{o,Zn} = 10 \ \mu A/cm^2$, $i_{o,H} = 10^{-3} \ \mu A/cm^2$, $\beta_a = 0.08 \ V$, $\beta_c = 0.12 \ V$, $T = 25^oC$.

Solution:

The possible half-cell reactions and their respective standard potential are

$$
\begin{array}{lll}
Zn \rightarrow Zn^{+2} + 2e & \Longrightarrow & E_{Zn} = -0.80 \ V \\
2H^+ + 2e \rightarrow H_2 & \Longrightarrow & E_H = ? \\
\hline
Zn + 2H^+ \rightarrow Zn^{+2} + H_2 & \Longrightarrow & E = E_{Zn} + E_H
\end{array}
$$
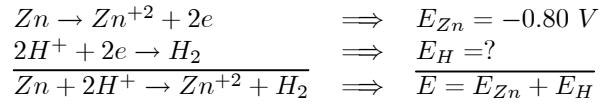
The activity of hydrogen ions and the hydrogen potential are, respectivily

$$pH = -\log\left[H^+\right]$$

$$\left[H^+\right] = 10^{-pH} = 10^{-4} \ \text{mol/l}$$

$$E_H = 0.059pH = 0.059\,(4) = 0.24 \ V$$

Using the definition of overpotential along with the condition $\eta_a = \eta_c$ yields

$$\eta_a = E - E_{Zn} = \beta_a \log\left(\frac{i_{corr}}{i_{o,Zn}}\right)$$

$$\eta_c = E - E_H - \beta_c \log\left(\frac{i_{corr}}{i_{o,H}}\right)$$

$$E_{Zn} + \beta_a \log\left(\frac{i_{corr}}{i_{o,Zn}}\right) = E_H - \beta_c \log\left(\frac{i_{corr}}{i_{o,H}}\right)$$

which leads to

$$\log\left(i_{corr}\right) = \frac{1}{\beta_a + \beta_c}\left[-E_{Zn} + E_H + \beta_a \log\left(i_{o,Zn}\right) + \beta_c \log\left(i_{o,H}\right)\right]$$

$$\log\left(i_{corr}\right) = \tfrac{1}{0.08 + 0.12}\left[-\left(-0.80\right) + 0.236 + 0.08\log\left(10\right) + 0.12\log\left(10^{-3}\right)\right]$$

$$\log\left(i_{corr}\right) = 1.40$$
$$i_{corr} = 10^{1.40}\ \mu A/cm^2 = 25.12\ \mu A/cm^2$$

From eq. (5.48),

$$C_R = \frac{i_{corr}A_w}{zF\rho} = \frac{\left(25.12x10^{-6}\ A/cm^2\right)\left(65.37\ g/mol\right)}{\left(2\right)\left(96,500\ A.s/mol\right)\left(7.14\ g/cm^3\right)}$$
$$C_R = 1.192x10^{-9}\ cm/s = 0.38\ mm/y$$
$$C_R = \frac{x}{t}$$
$$t = \frac{x}{C_R} = \frac{0.15\ mm}{0.38\ mm/y} = 0.40\ years = 146\ days$$

5.6   Calculate the activity and the corrosion rate of iron (Fe) immersed in an aerated aqueous solution of $pH = 9$. The dissociation constant for ferrous hydroxide, $Fe\left(OH\right)_2$, is $1.64x10^{-14}$. Given data:

$i_{o,Fe} = 10^{-2}\ \mu A/cm^2$ $\qquad E_{corr} = -0.30\ V$ $\qquad \beta_a = 0.10\ V$
$A_{w,Fe} = 55.85\ g/mol$ $\qquad \rho_{Fe} = 7.86\ g/cm^3$

Solution:

The possible half-cell reactions and standard potentials are

$Fe = Fe^{+2} + 2e$ $\qquad\qquad\qquad \Longrightarrow \quad E^o_{Fe} = 0.440\ V$
$\frac{1}{2}O_2 + H_2O + 4e = 2OH^-$ $\qquad \Longrightarrow \quad E^o_{H_2O} = -0.401\ V$
$Fe + \frac{1}{2}O_2 + H_2O = Fe^{+2} + 2OH^-$ $\quad \Longrightarrow \quad E^o = E^o_{Fe} + E^o_{H_2O} = 0.039\ V$
$Fe^{+2} + 2OH^- = Fe\left(OH\right)_2$ $\qquad\qquad\qquad E^o_{Fe(OH)_2} = 0.039\ V$
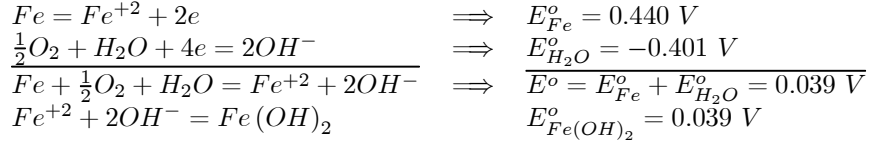
Thus, the oxidation of iron may be represented by the following reaction
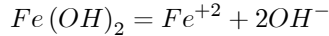
$$Fe\left(OH\right)_2 = Fe^{+2} + 2OH^-$$

From Table 2.6, $\left[OH^-\right] = 10^{pH-14} = 10^{-5}\ mol/l$ *so that the activity of ferrous iron becomes*

$$K_{Fe(OH)_2} = \frac{\left[Fe^{+2}\right]\left[OH^-\right]^2}{\left[Fe\left(OH\right)_2\right]}$$
$$\left[Fe^{+2}\right] = \frac{\left[Fe\left(OH\right)_2\right]K_{Fe(OH)_2}}{\left[OH^-\right]^2} = \frac{\left[1\right]\left(1.64x10^{-14}\right)}{\left[10^{-5}\right]^2}$$
$$\left[Fe^{+2}\right] = 1.64x10^{-4}\ mol/l$$

Using eq. (5.32) gives the corrosion density

$$
\begin{aligned}
\eta_a &= E_{corr} - E^o_{Fe(OH)_2} = -0.30\ V - 0.039\ V \\
\eta_a &= -0.339\ V \\
\eta_a &= \beta_a \log\left(\frac{i_{corr}}{i_{o,Fe}}\right) \\
\log\left(\frac{i_{corr}}{i_{o,Fe}}\right) &= -\frac{0.339\ V}{0.10\ V} = -3.39 \\
i_{corr} &= i_{o,Fe}10^{-3.39} = \left(10^{-8}\ A/cm^2\right)\left(10^{-3.39}\right) \\
i_{corr} &= 4.07x10^{-12}\ A/cm^2
\end{aligned}
$$

From eq. (5.48), the corrosion rate is

$$
\begin{aligned}
C_R &= \frac{i_{corr}A_w}{zF\rho} = \frac{\left(4.07x10^{-12}\ A/cm^2\right)(55.85\ g/mol)}{(2)\left(96,500\ A.s/mol\right)\left(7.86\ g/cm^3\right)} \\
C_R &= 1.50x10^{-16}\ cm/s = 4.73x10^{-8}\ mm/y = 0.0473\ \mu m/y
\end{aligned}
$$

5.7   Plot the anodic data given below and determine the polarization resistance (R_p) and the anodic Tafel slope (β_a) for a metal M. Use $\beta_c = 0.07\ V$ and $i_{corr} = 0.019\ A/cm^2$.

$M = M^{+2} + 2e^-$	$i\ \left(\mu A/cm^2\right)$	$E\ (V_{SHE})$
$2H^+ + 2e^- = H_2$	0.08	-0.32
	0.10	-0.30
	0.15	-0.25
	0.18	-0.22
	0.20	-0.20

Solution:

Linear least squares on the given data gives $E = -0.4\ V + \left(1.0V.cm^2/A\right)i$
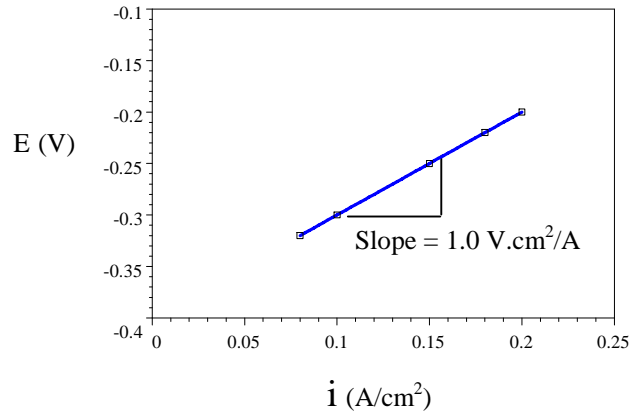
The polarization resistance and the anodic Tafel slope are

$$R_p = slope = 1.0 \ ohm.cm^2$$

$$R_p = \frac{\beta}{i_{corr}}$$

$$\beta = \frac{\beta_a \beta_c}{2.303 \left(\beta_a + \beta_c\right)} = 0.019 \ V$$

Thus,

$$\beta_a = 0.12 \ V$$

5.8 Why does a pearlitic steel corrode rapidly in an acidic solution?

Answer: *Because of the galvanic effects between the body-centered cubic ferrite (BCC α-Fe) and tetragonal cementite (Fe₃C) crystal structures. In fact, this type of corrosion is beneficial for revealing the steel microstructure.*

5.9 Why will the tip and the head of an iron nail behave as anodes relative to the shank? See Figure 1.10a.

Answer: *Because the tip and the head of the nail are highly strained areas containing large amounts crystal defects, such as dislocations, voids, and possibly microcracks. These areas contain large amounts of stored strain energy.*

5.10 It is known that the standard electrode potential (E^o) for pure crystalline zinc is $-0.763 \ V$. Will this value change by cold working and impurities? Explain.

Answer: *Cold working causes microstructural changes and crystal defects, which in turn change the mechanical properties and increases corrosion. On*

the other hand, impurities also change properties due to segregation along grain boundaries. Therefore, E^o must change and it is different at grain boundaries (atomic mismatch) due to the straining effects induced during cold working than the potential within grains. Consequently, the grain boundaries and possibly secondary phases become anodic sites to grains.

5.11 An electrolyte contains a very low activity $(8x10^{-9} \ mol/l)$ of silver cations (Ag^+) and an unknown concentration of copper cations. If the cell potential difference between the copper anode and the silver cathode is -0.04 V, determine a) which cation will be reduced (electroplated) on the cathode and b) the concentration of $\left[Cu^{+2}\right]$ in g/l at $40^o C$. Neglect the effects of other ions that might react with silver.

Solution:

The possible half-cell reactions and standard potentials are

$$
\begin{array}{lll}
2Ag^+ + 2e = 2Ag & \implies & E^o_{Ag} = 0.799 \ V \\
Cu = Cu^{+2} + 2e & \implies & E^o_{Cu} = -0.337 \ V \\
\hline
2Ag^+ + Cu = 2Ag + Cu^{+2} & \implies & E^o = E^o_{Ag} + E^o_{Cu} = 0.462 \ V
\end{array}
$$
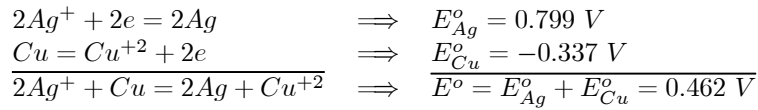
The free energy change is

$$
\begin{aligned}
\Delta G^o & = -zFE^o = -(2)(96,500 \ J/mol.V)(0.462 \ V) \\
\Delta G^o & = -89,166 \ J/mol
\end{aligned}
$$

Therefore, silver (Ag) will be reduced since $\Delta G^o < 0$. Using the Nernst equation yields the copper ion concentration

$$
\begin{aligned}
E & = E^o - \frac{RT}{zF}\ln(K) \\
\ln(K) & = \frac{zF(E^o - E)}{RT} = \frac{(2)\left(96,500 \ \frac{J}{mol.V}\right)(0.462 \ V + 0.04 \ V)}{\left(8.314 \ \frac{J}{mol.^o K}\right)(313^o K)} \\
\ln(K) & = 37.23 \\
K & = 1.48x10^{16}
\end{aligned}
$$

Then,

$$K = \frac{[Ag]^2 [Cu^{+2}]}{[Ag^+]^2 [Cu]}$$

$$[Cu^{+2}] = \frac{K [Ag^+]^2 [Cu]}{[Ag]^2}$$

$$[Cu^{+2}] = \frac{(1.48x10^{16}) [8x10^{-9} \ mol/l]^2 [1 \ mol/l]}{[1 \ mol/l]^2}$$

$$[Cu^{+2}] = 0.95 \ mol/l$$

$$C_{Cu^{+2}} = [Cu^{+2}] A_{w,Cu} = (0.95 \ mol/l)(63.55 \ g/mol)$$

$$C_{Cu^{+2}} \simeq 60 \ g/l$$

5.12 Suppose that a cold worked copper electrode has $8,000 \ J/mol$ stored energy and dissolves in an aqueous electrolyte. Calculate the overpotential.

Solution:

$$Cu = Cu^{+2} + 2e \implies E^o = -0.337 \ V$$
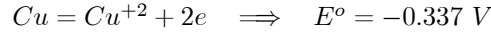
From eq. (2.24),

$$\Delta G = -zFE$$

$$E = -\frac{\Delta G}{zF} = -\frac{8,000 \ J/mol}{(2)(96,500 \ \frac{J}{mol.V})}$$

$$E = -0.042 \ V > E_{Cu}^o$$

$$\eta_a = E - E^o = -0.042 \ V - 0.337V$$

$$\eta_a \simeq -0.38 \ V$$

5.13 What is the significant differences between the overpotential (η) and the Ohmic potential (E)?

Answer: *Mathematically, both potentials have different physical trend. Thus, the overpotential is nonlinear with respect to the current or current density since $\eta = \beta \log (I/I_{corr})$. If $\eta \neq 0$, the anode electrode is polarized and η is a measure of the energy required for polarization since $\Delta G = -zF\eta$. On the other hand, Ohm's law, $E = IR$ is linear and it may include other terms, such as overpotential and solution (electrolyte) potential, $\phi_s = IR_s$. Equation (3.25) describes the Ohm's potential in details.*

$$E = E_{corr} - \eta_a - \eta_c - \phi_s = IR$$

5.14 If a sheet of zinc (Zn) is placed in hydrochloric acid (HCl), Zn goes into solution. Why?

Answer: *Localized anodic and cathodic areas must exist on the sheet surface so that the following reactions occur*

$$
\begin{array}{lll}
Zn = Zn^{+2} + 2e & \implies & E^o_{Zn} = 0.763 \ V \\
2H^+ + 2e = H_2 & \implies & E^o_H = 0 \\
\hline
Zn + 2H^+ = Zn^{+2} + H_2 & \implies & E^o = E^o_{Zn} + E^o_H = 0.763 \ V
\end{array}
$$
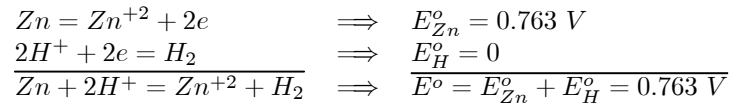
The standard free energy change must be $\Delta G^o < 0$ in order for the above reactions to occur. Using eq. (2.24) yields

$$
\begin{aligned}
\Delta G^o &= -zFE^o = -(2)(96,500 \ J/mol.V)(0.763 \ V) \\
\Delta G^o &= -147.26 \ kJ/mol
\end{aligned}
$$

5.15 Calculate the equilibrium constant at 25^oC for the electrochemical cell shown in Figure 2.4.

Solution:

Combining eqs. (2.24) and (2.31b) along with $E^o = 1.10 \ V$ gives

$$
\begin{aligned}
-zFE^o &= -RT\ln(K) \\
\ln(K) &= \frac{zFE^o}{RT} \\
\ln(K) &= \frac{(2)(96,500 \ J/mol.V)(1.10V)}{(8.314 \ J/mol.^oK)(298^oK)} = 85.69 \\
K &= 1.64x10^{37}
\end{aligned}
$$

5.16 Show that $\Delta G = zF\beta_a \log(i_a/i_{corr})$ where the local potential E can be defined by the Nernst equation.

Solution:

Using eqs. (3.31) and (2.24) yields

$$
\begin{aligned}
E &= E^o - \frac{RT}{zF}\ln(K) \\
\ln(K) &= \frac{zF(E^o - E)}{RT}
\end{aligned}
$$

But,

$$\Delta G = -RT \ln(K)$$
$$\Delta G = -RT.\frac{zF(E^o - E)}{RT}$$
$$\Delta G = zF(E - E^o) = zF\eta_a$$

But,

$$\eta_a = \beta_a \log\left(\frac{i_a}{i_{corr}}\right)$$
$$\Delta G = zF\beta_a \log\left(\frac{i_a}{i_{corr}}\right)$$

5.17 If an electrochemical cell operates at 10 *amps*, 25°*C*, and 101 *kPa* for 30 minutes, calculate a) the number of moles and b) the weight of copper would be produced.

Solution:

The reduction reaction is $Cu^{+2} + 2e = Cu$. *From eq.* (5.12b),

$$N = \frac{It}{zF} = \frac{(10\ A)(1,800\ s)}{(2)(96,500\ A.s/mol)} = 0.093 moles$$

From eq. (5.12c),

$$W = \frac{ItA_w}{zF} = NA_w = (0.093 mol)(63.55\ g/mol)$$
$$W = 5.93\ grams$$

5.18 **(a)** Derive the Arrhenius equation from the general definition of the activation energy of any rate reaction process, **(b)** determine the Arrhenius constants B and A_e using the derived equation and the following data for the dissociation constants: $K_{sp@300} = 10^{11}$, $K_{sp@350} = 3K_{sp@300}$ between $300°K$ and $350°K$. It is assumed that the activity coefficients approach 1 in diluted electrolyte solution and that K_{sp} follows an Arrhenius type trend. Recall that K_{sp} can be expressed in terms of concentrations. **(c)** Plot the given data below and draw the trend line in the close interval [200,400] for the temperature axis and [0,4]x10^{11} for the reaction constant K_{sp} axis.

T (°K)	Dissociation Constant K_{sp}
200	$0.02x10^{11}$
250	$0.22x10^{11}$
280	$0.50x10^{11}$
300	$1.00x10^{11}$
330	$1.95x10^{11}$
350	$3.00x10^{11}$
360	$3.65x10^{11}$

Solution:

(a) *From eq. (5.20),*

$$
\begin{aligned}
\Delta G^* &= RT^2 \frac{d\left(\ln K_{sp}\right)}{dT} \\
\frac{dT}{T^2} &= \frac{Rd\left(\ln K_{sp}\right)}{\Delta G^*} \\
\int_o^T T^{-2} dT &= \frac{R}{\Delta G^*} \int d\left(\ln K_{sp}\right) \\
-T^{-1} &= \frac{R}{\Delta G^*}\left(\ln K_{sp} - \ln B\right) \\
\ln \frac{K_{sp}}{B} &= -\frac{\Delta G^*}{RT} \\
K_{sp} &= B \exp\left(-\frac{\Delta G^*}{RT}\right)
\end{aligned}
$$

(b) *Using the derived expression for two different rates yields*

$$
\begin{aligned}
K_{sp@300} &= B \exp\left(-\frac{\Delta G^*}{RT_{300}}\right) \\
K_{sp@350} &= B \exp\left(-\frac{\Delta G^*}{RT_{350}}\right) \\
\frac{K_{sp@300}}{K_{sp@350}} &= \exp\left[\frac{\Delta G^*}{RT}\left(\frac{1}{T_{350}} - \frac{1}{T_{300}}\right)\right]
\end{aligned}
$$

Thus,

$$
\begin{aligned}
\Delta G^* &= \frac{R\ln\left(K_{sp@300}/K_{sp@350}\right)}{1/T_{350} - 1/T_{300}} \\
\Delta G^* &= \frac{(8.314)\ln(1/3)}{1/350 - 1/300} = 19,181 \text{ J/mol}
\end{aligned}
$$

and

$$
\begin{aligned}
B &= K_{sp@300} \exp\left(\frac{\Delta G^*}{RT_{300}}\right) \\
B &= \left(10^{11}\right) \exp\left\{-\frac{19181 \text{ J/mol}}{[8.314 \text{ J/(mol.K)}](300 \text{ K})}\right\} \\
B &= 2.1869 \times 10^{14}
\end{aligned}
$$

Check:

$$
\begin{aligned}
K_{sp@300} &= B \exp\left(-\frac{\Delta G^*}{RT_{300}}\right) \\
K_{sp@300} &= \left(2.1869 \times 10^{14}\right) \exp\left(-\frac{19181}{(8.314)\,(300)}\right) = 1 \times 10^{11} \\
K_{sp@350} &= \left(2.1869 \times 10^{3}\right) \exp\left(-\frac{19181}{(8.314)\,(350)}\right) = 3 \times 10^{11} \\
\frac{K_{sp@350}}{K_{sp@300}} &= \frac{3 \times 10^{11}}{1 \times 10^{11}} = 3
\end{aligned}
$$

(c) Plot $K_{sp} = \left(2.1869 \times 10^3\right) \exp\left(-\frac{19181}{8.314T}\right) = 2186.9 \exp\left(-\frac{2307.1}{T}\right)$
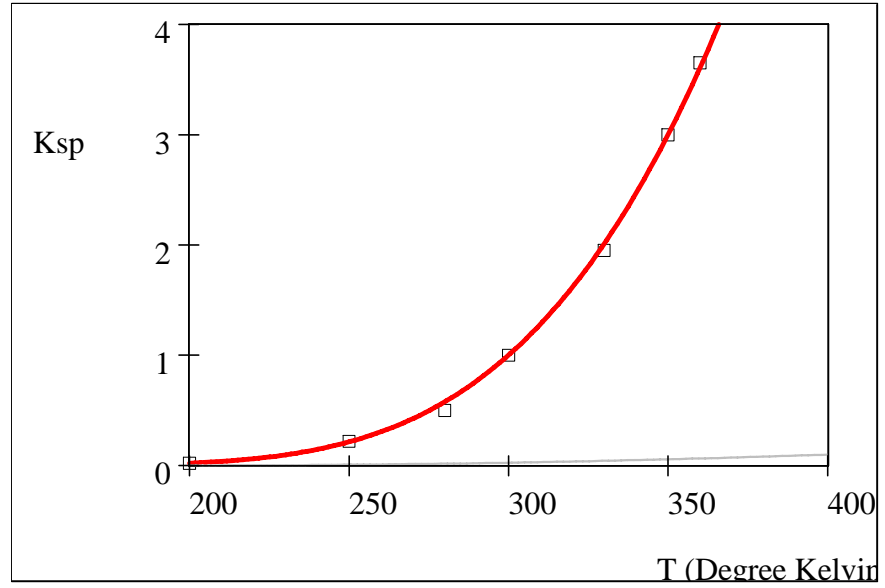
5.19 Plot the given conductivity data *vs.* the aqueous $Cu^{+2}SO_4^{-}$ concentration at $25^{o}C$ and $1\ atm$. (The data was taken from Ref. [5]). Conduct a nonlinear regression analysis on these data and explain the resultant curve.

C $\left(mol/cm^3\right)$ $x10^{-6}$	K_c $\left(ohm^{-1} \cdot cm^{-1}\right)$ $x10^{-3}$
0	0
25.00	3.00
50.00	5.10
75.00	7.40
100.00	8.50
102.50	10.00
200.00	15.00
202.50	16.00

Linear least squares on the given data yields

$$K_c = \left(1.1922x10^{-3}\ ohm^{-1} \cdot cm^{-1}\right) + \left(73.46\ mol/cm^3\right) C$$
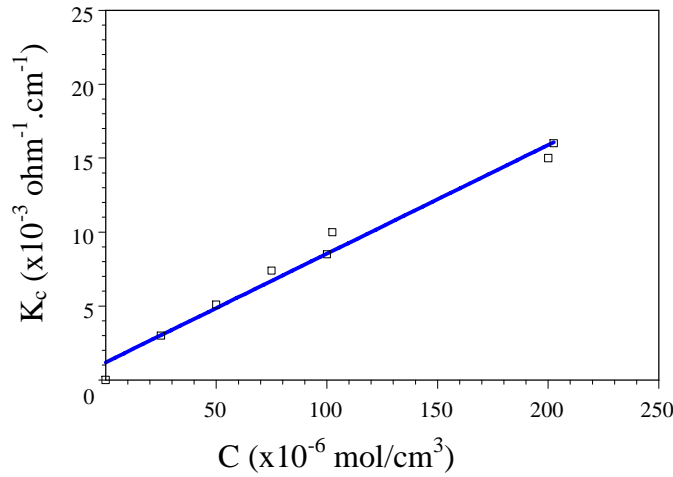
In fact, $Cu^{+2}SO_4^-$ solution is a weak electrolyte due to the interactions among Cu^{+2} and SO_4^- ions. However, K_c increases because the number of charge carriers per unit volume increase with the electrolyte concentration.

5.20 An electrochemical cell operates at a small overpotential and the corroding metal is exposed to a H^+ ion-containing electrolyte. Use the given data

$\eta = 0.005\ V$	$T = 25^oC$
$i = 3.895 \times 10^{-8}\ A/cm^2$	$\rho = 7.14\ g/cm^3$
$i_o = 10^{-7}\ A/cm^2$	$D = 10^{-5}\ cm^2/s$
$C_R = 5.8277x10^{-4}\ mm/y$	

in order to determine a) the corroding metal by calculating the atomic weight A_w and determining its anodic reaction. Assume that there is a linear relationship between the current density and the overpotential. b) The activity of the corroding metal if $a_{H^+} = 1 \ mol/l$, c) the free energy change ΔG. Will the reaction you have chosen occur?, d) the ionic velocity of the corroding metal. As a crude approximation, neglect the ionic velocity of other ions in solution. e) The ionic mobility B and f) electrolyte conductivity by neglecting other ions present in the electrolyte.

Solution:

a) From eq. (5.16c),

$$i = i_o \left(\frac{zF\eta}{RT} \right) \tag{3.16c}$$

$$z = \frac{iRT}{i_o F\eta} = \frac{\left(3.895x10^{-8} \ A/cm^2\right)\left(8.314 \ J/mol.^oK\right)\left(298^oK\right)}{\left(10^{-7} \ A/cm^2\right)\left(96,500 \ J/mol.V\right)\left(0.005 \ V\right)}$$

$$z = 2$$

Using eq. (5.48) yields

$$C_R = \frac{iA_w}{zF\rho} = 5.8277x10^{-4} mm/y = 1.848x10^{-12} \ cm/s \tag{3.48}$$

$$A_w = \frac{zF\rho C_R}{i} = \frac{(2)\left(96,500 \ A.s/mol\right)\left(7.139 \ g/cm^3\right)\left(1.848x10^{-12} \ cm/s\right)}{\left(3.895 \times 10^{-8} \ A/cm^2\right)}$$

$$A_w = 65.38 \ g/mol$$

Therefore, the corroding metal is zinc and its anodic reaction is

$$Zn = Zn^{+2} + 2e$$
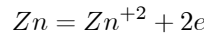
b) According to the results obtained in part a), the reactions and potentials taking place at 25^oC are

$$
\begin{array}{lll}
Zn = Zn^{+2} + 2e & \Longrightarrow & E^o_{Zn} = 0.763 \ V \\
2H^+ + 2e = H_2 & \Longrightarrow & E^o_H = 0 \\
\hline
Zn + 2H^+ = Zn^{+2} + H_2 & \Longrightarrow & E^o = E^o_{Zn} + E^o_H = 0.763 \ V
\end{array}
$$
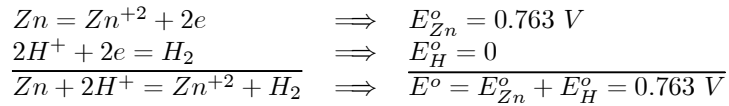
Using the Nernst equation, eq. (2.32), along with $\eta = E - E^o = 0.005 \ V$ gives the activity of Zn^{+2} ions

$$E = E^o - \frac{RT}{zF} \ln(K) \tag{2.32}$$

$$\eta = -\frac{RT}{zF} \ln \frac{\left[Zn^{+2}\right][H_2]}{[Zn][H^+]^2}$$

$$\left[Zn^{+2}\right] = \frac{[Zn][H^+]^2}{[H_2]} \exp\left[-\frac{zF\eta}{RT}\right]$$

$$\left[Zn^{+2}\right] = \frac{[1\ mol/l][1\ mol/l]^2}{[1\ mol/l]} \exp\left[-\frac{(2)(96,500\ J/mol.V)(0.005\ V)}{(8.314\ J/mol.^oK)(298^oK)}\right]$$

$$\left[Zn^{+2}\right] = 0.677\ mol/l = 6.77x10^{-4}\ mol/cm^3$$

c) From eq. (2.24),

$$\Delta G = -zFE \tag{2.24}$$

$$E = \eta + E^o = 0.005\ V + 0.763V = 0.768\ V$$

$$\Delta G = -(2)(96,500\ J/mol.V)(0.768\ V)$$

$$\Delta G = -148.224\ kJ/mol$$

Therefore, the above reactions occur because $\Delta G < 0$.

d) Using eq. (5.95) yields the zinc ionic velocity

$$i = zFv_jC_j = zFv_{Zn^{+2}}C_{Zn^{+2}} = zFv_{Zn^{+2}}\left[Zn^{+2}\right] \tag{3.95}$$

$$v_{Zn^{+2}} = v_j = \frac{i}{zFC_{Zn^{+2}}}$$

$$v_{Zn^{+2}} = \frac{(3.895x10^{-8}\ A/cm^2)}{(2)(96,500\ A.s/mol)(6.77x10^{-4}\ mol/cm^3)}$$

$$v_{Zn^{+2}} = 2.98x10^{-10}\ cm/s$$

e) Using eq. (5.97) yields the zinc ionic mobility

$$D_{Zn^{+2}} = kTB_{Zn^{+2}} \tag{3.97}$$

$$B_{Zn^{+2}} = \frac{D_{Zn^{+2}}}{kT} = \frac{10^{-5}\ cm^2/s}{(1.38x10^{-23}\ J/mol.^oK)(298^oK)}$$

$$B_{Zn^{+2}} = 2.43x10^{15}\ \frac{cm^2.mol}{J.s} = 2.43x10^{15}\ \frac{cm^2}{V.s}$$

f) Using eq. (5.93) gives the zinc ionic conductivity

$$K_{c,Zn^{+2}} = zFB_{Zn^{+2}}C_{Zn^{+2}}$$

$$K_{c,Zn^{+2}} = (2)(96,500\ A.s/mol)\left(2.43x10^{15}\ \frac{cm^2}{V.s}\right)(6.77x10^{-4}\ mol/cm^3)$$

$$K_{c,Zn^{+2}} = 3.18x10^{17}\ ohm^{-1}.cm^{-1}$$

5.21 If an electrochemical copper reduction process is carried out at 5 *amperes.* for 20 *minutes*, determine a) the electric charge (amount of coulombs of electricity), b) the number of electrons if there are $1/\left(1.6022x10^{-19}\right) = 6.24x10^{18}$ *electron/C*, c) the number of moles, d) Faraday's weight reduced on a cathode, and the reduction rate (production rate in Chapter 7). Data: $A_w = 63.55$ *g/mol* and $T = 35^oC$.

Solution:

a) The reactions and potentials taking place at 35^oC are

$$
\begin{array}{lll}
Cu = Cu^{+2} + 2e & \implies & E_{Cu}^o = 0.337 \ V \\
2H^+ + 2e = H_2 & \implies & E_H^o = 0 \\
\hline
Cu + 2H^+ = Cu^{+2} + H_2 & \implies & E^o = E_{Cu}^o + E_H^o = 0.763 \ V
\end{array}
$$
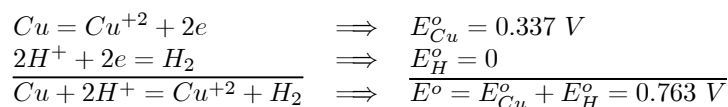
From eq. (5.12a),

$$Q = It = (5 \ A)(1,200 \ s) = 6,000 \ C$$

b)

$$
\begin{aligned}
N_e & = (6,000 \ C)\left(6.24x10^{18}electron/C\right) \\
N_e & \simeq 4x10^{22} \ electrons
\end{aligned}
$$

c) From eq. (5.12b),

$$N = \frac{Q}{zF} = \frac{6,000 \ C}{(2)(96,500 \ C/mol)} = 0.0311 \ moles$$

d) From eq. (5.12c),

$$
\begin{aligned}
W & = NA_w = (0.0311 \ moles)(63.55 \ g/mol) \\
W & = 1.98 \ grams
\end{aligned}
$$

e)

$$P_R = \frac{W}{t} = \frac{1.98 \ g}{1,200 \ s} = 1.65x10^{-3} \ g/s = 5.94 \ g/h$$

5.22 Calculate the overpotential that causes hydrogen evolution on a flat platinum (Pt) electrode surface immersed in an acid solution, when the applied cathodic and exchange current densities are 6,000 $\mu A/cm^2$ and 100 $\mu A/cm^2$, respectively. Assume a symmetry factor of 0.50 at room temperature (25^oC).

Solution:

$$2H^+ + 2e = H_2 \implies E_H^o = 0$$
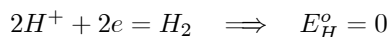
From eq. (5.20b),

$$\eta_c = -\frac{RT}{zF\alpha}\ln\left(\frac{i_c}{i_o}\right)$$

$$\eta_c = -\frac{\left(8.314 \frac{J}{mol.^oK}\right)(298^oK)}{(1)(96,500 \ J/mol.V)(0.5)}\ln\left(\frac{6,000}{100}\right)$$

$$\eta_c = -0.21V$$

5.23   Consider a discharge (chemical desorption) mechanism as the rate determining for $Ni^{+2} + 2e^- = Ni$ at 25^oC in a nickel battery. Calculate the cathodic Tafel slope per decade if the symmetry factor is 0.50, the exchange current density is constant, and the cathodic overpotential is $\eta_c < 0$.

Solution:

From eq. (5.20b),

$$\eta_c = -\frac{RT}{zF\alpha}\ln\left(\frac{i_c}{i_o}\right)$$

$$\eta_c = -\frac{2.303RT}{zF\alpha}\log\left(\frac{i_c}{i_o}\right)$$

$$\frac{d\eta_c}{d\log(i_c)} = -\frac{2.303RT}{zF\alpha}$$

Thus,

$$\beta_c = \frac{d\eta_c}{d\log(i_c)} = -\frac{(2.303)\left(8.314 \frac{J}{mol.^oK}\right)(298^oK)}{(2)(96,500 \ J/mol.V)(0.5)}$$

$$\beta_c = -0.06 \ V/decade$$

5.24 Plot the normalized current profile as a function of both symmetry factor (α) and overpotential; that is, $i/i_o = f(\alpha, \eta)$ when the oxidation state is defined is $z = 2$ and $\alpha = 0.35$, 0.50 and 0.75 at room temperature (25^oC). Explain the polarization behavior very succinctly.

Solution:

Using eq. (5.16) yields

$$\frac{i}{i_o} = \exp\left[\frac{\alpha zF\eta}{RT}\right] - \exp\left[-\frac{(1-\alpha)zF\eta}{RT}\right]$$

$$\frac{i}{i_o} = \exp[77.90\alpha\eta] - \exp[-(1-\alpha)77.90\eta]$$
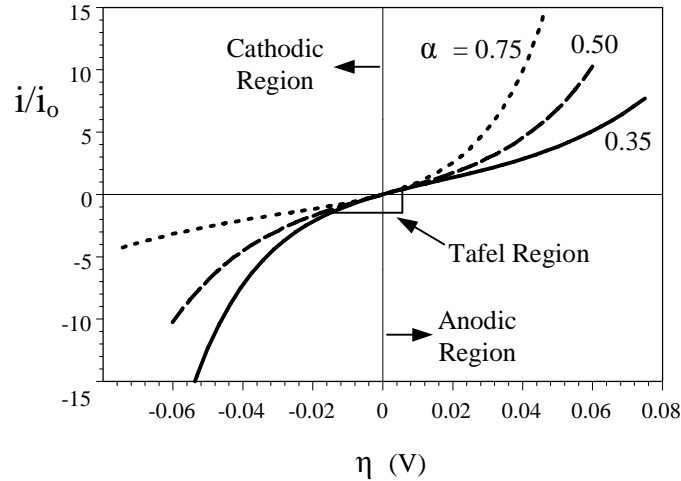
The normalized current density (i/i_o) shows the expected linearized Tafel region at small values of the anodic and cathodic overpotentials (η). However, the departure from this linearity is obvious at large η and the shape of the curves change significantly. Therefore, variations of the current density (i) strongly depend on the overpotential (η) and the shape of the curves depend on the symmetry factor (α). The slopes of the curves at large η are characteristics of α since it arises due to changes in the electric double layer structure.

5.25 *Calculate the mass and number of moles a) of a battery zinc (Zn) casing and b) of the manganese dioxide (MnO_2) in the electrolyte if the battery has a stored energy of 36 kJ/V and a power of 3 Watts. c) Find the time it takes to consume the stored energy if the battery operates at a current of 2 A and the potential (voltage). The thickness of the cell is $x = 1$ mm and other dimensions are indicated below. The discharging reaction is*

$$MnO_2 + H^+ + e \rightarrow MnOOH$$
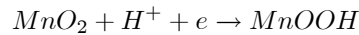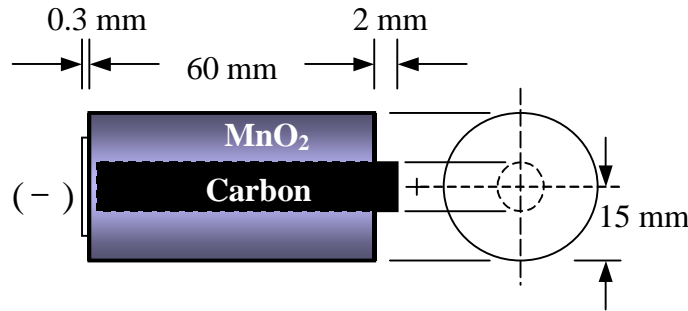
Solution:

$Q = 36 \ kJ/V = 36,000 \ A.s = 36,000 \ Coulombs$

$A_s = 2\pi Lr = (2\pi)(6 \ cm)(1.5 \ cm) = 56.55 \ cm^2$

$V = xA_s = (0.1 \ cm)(5.6549 \ cm^2) = 5.65 \ cm^3$

a) The mass and moles of Zn

$$M_{Zn} = V\rho = (5.65 \ cm^3)(7.14 \ g/cm^3) = 40.34 \ g$$

$$X_{Zn} = \frac{M_{Zn}}{A_{w,Zn}} = \frac{40.34 \ g}{65.37 \ g/mol} = 0.62 \ mol$$

b) The mass and moles of MnO_2 are

$$X_{MnO_2} = \frac{Q}{zF} = \frac{36,000 \ A.s}{(1)(96,500 \ A.s/mol)}$$

$$X_{MnO_2} = 0.37 \ mol$$

$$M_{MnO_2} = X_{MnO_2} A_{w,MnO_2} = (0.37 \ mol)(86.94 \ g/mol)$$

$$M_{MnO_2} = 32.17 \ g$$

c) The time for discharging the stored energy is

$$t = \frac{Q}{I} = \frac{36,000 \ A.s}{2 \ A} = 5 \ hours$$

$$E = P/I = (3 \ V.A)/(2 \ A) = 1.5 \ V$$

5.26 A plate of pure nickel (Ni) oxidizes in an electrochemical cell containing an acid solution at 25^oC. The total surface area of the nickel plate is 100 cm^2. If $2x10^{16}$ electrons per second (e/s) are relieved on the plate surface, then calculate a) the corrosion rate in mm/y and b) the mass of nickel being lost in a year..

Solution:

$Ni = Ni^{+2} + 2e$	$z = 2$	$\rho = 8.90 \ g/cm^3$
$r = 2x10^{16} \ e/s$		$A_w = 58.71 \ g/mol$
$q_e = 1.6022x10^{-19} \ A.s/e$		$A_s = 100 \ cm^2$

a) From eq. (5.50),

$$\begin{aligned} I &= rq_e = \left(2x10^{16} \ e/s\right)\left(1.6022x10^{-19}A.s/e\right) \\ I &= 3.20x10^{-3} \ A \\ i &= \frac{I}{A_s} = \frac{3.20x10^{-3} \ A}{100cm^2} = 32 \ \mu A/cm^2 \end{aligned}$$

Then,

$$\begin{aligned} C_R &= \frac{iA_w}{zF\rho} = \frac{\left(32x10^{-6} \ A/cm^2\right)(58.71g/mol)}{(z)\left(96,500 \ A.s/mol\right)\left(8.90g/cm^3\right)} \\ C_R &= 1.10x^{-9} \ cm/s = 0.35 \ mm/y \end{aligned}$$

b)

$$\begin{aligned} i &= \frac{I}{A_s} = \frac{zFm}{A_stA_w} \\ \frac{zFm}{A_stA_w} &= \frac{zF\rho C_R}{A_w} \\ m &= \rho C_R A_s t = \left(8.90 \ g/cm^3\right)(0.035 \ cm/s)\left(100 \ cm^2\right)(1 \ y) \\ m &= 31.15 \ grams \end{aligned}$$

5.27   Use the data listed in Table 3.3 to perform a least squares analysis and subsequently, determine the polarization proportionality constant β. Let the atomic weight and the density of the steel be $A_{w,steel} = A_{w,Fe} = 55.85$ g/mol and $\rho = 7.85 \ g/cm^3$, respectively.

Solution:

Curve fitting:

$$R_p = 3.8502 \times 10^{-2} \ ohm.cm^2 + \left(30.147 \ \frac{ohm.cm^3}{y}\right)\frac{1}{C_R}$$
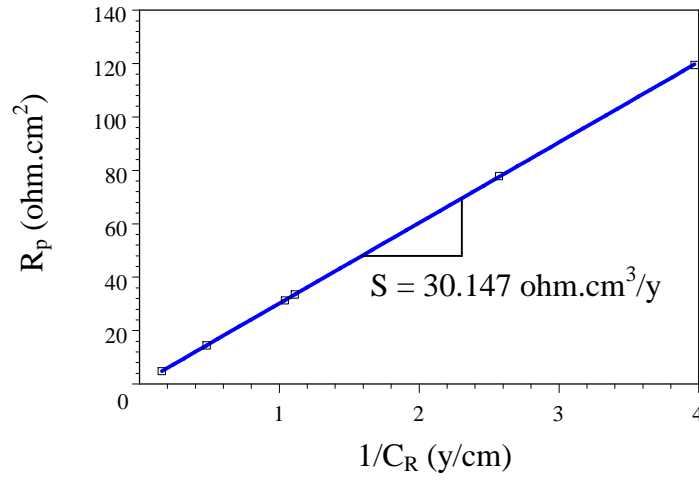
Combining eqs. (3.25a) and (3.48) yields

$$R_p = \left(\frac{\beta A_w}{zF\rho}\right)\frac{1}{C_R}$$

$$S = \left(\frac{\beta A_w}{zF\rho}\right)$$

$$\beta = \frac{zF\rho S}{A_w} = \frac{(2)\left(3.06x10^{-3}\ A.y/mol\right)\left(7.85\ g/cm^3\right)\left(30.147\ ohm.cm^3/y\right)}{55.85\ g/mol}$$

$$\beta = 0.03\ V$$

5.28 Equal amounts of $CuSO_4$ and $NiSO_4$ are dissolved with water to make up an electrolyte. Hypothetically, the ion velocities and concentrations are

$$v_{Cu^{+2}} = 0.22\ cm/s \qquad C_{Ni^{+2}} = 10^{-5}\ mol/cm^3$$
$$v_{SO_4^{-2}} = 0.1\ cm/s \qquad C_{SO^{-2}} = 10^{-5}\ mol/cm^3$$
$$C_{Cu^{+2}} = 10^{-5}\ mol/cm^3$$

If the current density is $1\ A/cm^2$, calculate the velocity of the nickel ions $\left(Ni^{+2}\right)$.

Solution:

From eq. (5.86),

$$i = \sum z_j^+ F v_j^+ C_j^+ + \sum |z_j^-| F v_j^- C_j^-$$

$$i = F\left[(zvC)_{Cu^{+2}} + (zvC)_{Ni^{+2}} + (|z|\, vC)_{SO_4^{-2}}\right]$$

$$i = 2F\left[(vC)_{Cu^{+2}} + (vC)_{Ni^{+2}} + (vC)_{SO_4^{-2}}\right]$$

If $z_{Cu^{+2}} = z_{Ni^{+2}} = \left|z_{SO_4^{-2}}\right| = 2$ *and* $C = C_{Cu^{+2}} = C_{Ni^{+2}} = C_{SO_4^{-2}} = 10^{-5}$ *mol/cm*^{3}*, then*

$$i = 2FC\left[v_{Cu^{+2}} + v_{Ni^{+2}} + v_{SO_4^{-2}}\right]$$

Solving for $v_{Ni^{+2}}$ *yields*

$$v_{Ni^{+2}} = \frac{i}{2CF} - v_{Cu^{+2}} - v_{SO_4^{-2}}$$

$$v_{Ni^{+2}} = \frac{1}{(2)\left(10^{-5}\frac{mol}{cm^3}\right)\left(96,500\,\frac{A.s}{mol}\right)} - 0.22\,\frac{cm}{s} - 0.1\,\frac{cm}{s}$$

$$v_{Ni^{+2}} = 0.20\ cm/s$$

5.29 An electrochemical cell operates at 10 A, $R_x = 0.25\ ohm$, and $\omega = 50$ Hz. Determine a) the electrolyte resistance (R_s), b) the potential E_x when the external resistance and the capacitance are $R_x = 0.25\ ohm$ and $C_x = 20\ A.s/V$ at 30^0C and c) the electrolyte conductivity K_c. The distance between electrodes is $L = 15\ cm$ and the effective electrode surface is $A = 8,000\ cm^2$.

Solution:

a) From eq. (5.103),

$$Z(w)_x = \sqrt{R_x^2 + \left(\frac{1}{\omega C_x}\right)^2}$$

$$Z(w)_x = \sqrt{(0.25\ ohm)^2 + \left[\frac{1}{(50\ s^{-1})(20A.s/V)}\right]^2}$$

$$Z(w)_x = 0.25\ ohm$$

Therefore, $R_s = Z(w)_x = 0.25\ ohm$.

b) From eq. (5.104),

$$E_x = I_x Z(w)_x$$

$$E_x = (10\ A)(0.25\ ohm) = 2.5\ V$$

c) From eq. (5.99),

$$
\begin{aligned}
\lambda &= L/A = (15 \ cm) / \left(8,000 \ cm^2\right) \\
\lambda &= 1.88x10^{-3} \ cm^{-1} \\
K_c &= \frac{\lambda}{R_s} = \frac{\lambda}{Z\left(w\right)_x} \\
K_c &= \frac{1.88x10^{-3} \ cm^{-1}}{0.25 \ ohm} = 7.50x10^{-3} \ ohm^{-1}.cm^{-1}
\end{aligned}
$$

5.30 Determine and analyze the impedance profile by varying the angular frequency for fixed $R_x = 0.25 \ ohm$ and $C_x = 20 \ A.s/V$.

Solution:

This problem requires use of eq. (5.103). The intent here is to show how the impedance depends on the angular frequency at very low values.

$$
Z\left(w\right)_x = \sqrt{(0.25)^2 + \left[\frac{1}{20\omega}\right]^2}
$$
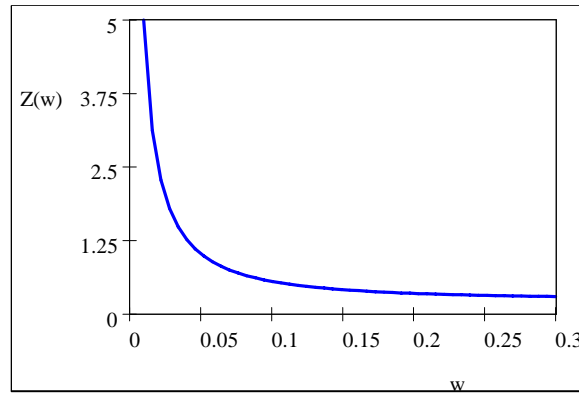
5.31 Assume that an electrolytic cell is used for recovering magnesium from a solution containing $10^{-4} \ mol/cm^3$ of Mg^{+2} at 35^0C. The nickel ionic mobility and the electric-field strength are $B = 55x10^{-5} \ cm^2V^{-1}s^{-1}$ and $F_x = 10 \ V/cm$ [Taken from reference 5], respectively, calculate **(a)** the ionic velocity (v), **(b)** the solution electric conductivity (K_c) and the electric resistivity (ρ_c). [Solution: (a) $v = 0.0055 \ cm/s$, (b) $K_c = 0.0106 \ ohm^{-1}.cm^{-1}$ and (c) $\rho_c = 94.21 \ ohm.cm$].

Solution:

a) From eq. (5.92),

$$v = BF_x = \left(55x10^{-5} \ \frac{cm^2}{V.s}\right)\left(10 \ \frac{V}{cm}\right) = 0.0055 \ cm/s$$

b) Using eq. (5.93) yields

$$
\begin{aligned}
K_c &= zFBC \\
K_c &= (2)\left(96,500 \ \frac{A.s}{mol}\right)\left(55x10^{-5} \ \frac{cm^2}{V.s}\right)\left(10^{-4} \ \frac{mol}{cm^3}\right) \\
K_c &= 0.0106 \ ohm^{-1}.cm^{-1}
\end{aligned}
$$

and from eq. (5.89)

$$\rho_c = 1/K_c = 94.21 \ ohm.cm$$

5.32 It is known that current flows when there exists a gradient of electric potential $(d\phi/dx)$ within an electric conductor, such as an electrolyte. Consider a current-carrying homogeneous conductor with constant cross-sectional area (A_c) so that the electric-field strength (E_x) is constant at every point in the conductor. Derive an expression for the current as a function of the gradient of electric potential. In this particular problem "x" stands for direction as well as length of the electric conductor. Start with the following current density definition $i = K_c E_x$, where K_c is the electric conductivity $(ohm^{-1}.cm^{-1})$.

Solution:

Using eq. (2.2a) and the given current density equation yields

$$E_x = -\frac{d\phi}{dx} \tag{a}$$

$$i = K_c E_x = -K_c \frac{d\phi}{dx} \tag{b}$$

$$\frac{I}{A_c} = -K_c \frac{d\phi}{dx} \tag{c}$$

$$I = -A_c K_c \frac{d\phi}{dx} \tag{d}$$

This expression agrees with the above statement because $I = f(d\phi/dx)$. For a homogeneous conductor, eq. (d) becomes

$$I = -A_c K_c \frac{\Delta\phi}{\Delta x}$$

where Δx becomes the length of the conductor.

EXTRA

5.EX1 *Determine the atomic weight of 82Mg-10Al-8Zn alloy.*

Solution:

The state of oxidation and the atomic weight of each element are

$$
\begin{aligned}
z_{Mg} &= 2 \quad \& \quad A_{w,Mg} = 24.31 \ g/mol \\
z_{Al} &= 3 \quad \& \quad A_{w,Al} = 26.98 \ g/mol \\
z_{Zn} &= 2 \quad \& \quad A_{w,Zn} = 65.37 \ g/mol
\end{aligned}
$$

From the given weight percent of the alloy, the weight fraction for Mg, Al and Zn are

$$
f_{Mg} = 0.82 \quad f_{Al} = 0.10 \quad f_{Zn} = 0.08
$$

Then the atomic weight of the alloy is

$$
\begin{aligned}
A_{w,alloy} &= \sum \frac{f_j A_{w,j}}{z_j} = \frac{f_{Mg} A_{w,Mg} + f_{Al} A_{w,Al} + f_{Zn} A_{w,Zn}}{z_{Mg} + z_{Al} + z_{Zn}} \\
A_{w,alloy} &= 13.48 \ g/mol
\end{aligned}
$$

5.EX2 *An electrochemical ionic concentration cell shown below was used as a concentration cell in order to measure the current due to the difference in ionic concentration between the anodic half-cell and the cathodic-half cell. Determine the corrosion rate in terms of electrons/second and the number of anodic reactions/second if the measured current is $3.23x10^{-7} \ \mu A = 3.23x10^{-7} C/s$.*
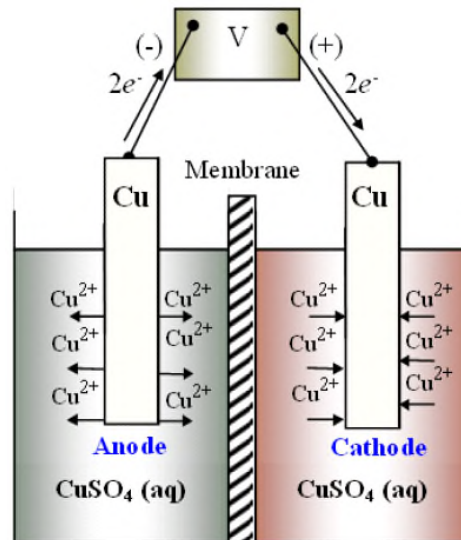
Solution:

The oxidation of copper (corrosion) and the reduction of copper (electroplating) are, respectively

$$Cu \longrightarrow Cu^{2+} + 2e^-$$
$$Cu^{2+} + 2e^- \longrightarrow Cu$$
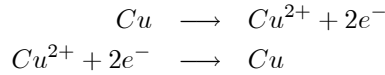
Clearly, the oxidation state is $z = 2$. Thus, the corrosion rate is

$$r = \frac{I}{q_e} = \frac{3.23x10^{-7}C/s}{(1.6022x10^{-19}~C/electrons)} \approx 2x10^{12}~electrons/s$$

Also,

$$r = \frac{I}{zq_e} = \frac{3.23x10^{-7}C/s}{\left(2~\frac{electrons}{reactions}\right)(1.6022x10^{-19}~C/electrons)}$$
$$r = 10^{12}~reactions/s$$

5.EX3 Use the Evans diagram given below to determine (a) the linear corrosion rate profile, $C_R = f(i_x)$, at $10^{-8}~A/cm^2 \le i_x \le 10^{-3}~A/cm^2$ and (b) the non-linear counterpart, $C_R = f(E_a)$, at $-0.45~V \le E_a \le -0.25~V$ for iron (Fe) immersed in a acid solution. Use C_R in units mm/yr and let i_x be the applied current density. The atomic weight and density of iron are $A_w = 55.85~g/mol$ and $7.87~g/cm^3$, respectively. Explain.
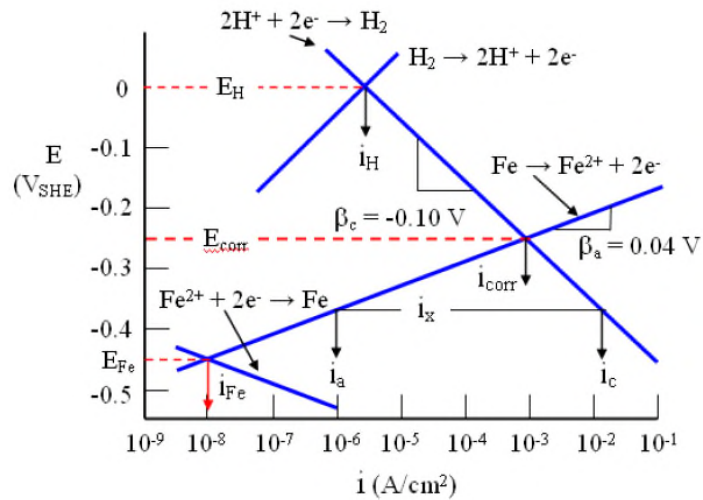
Solutions:

(a) *From* eq. (5.48),

$$C_R = \frac{i_a A_w}{zF\rho} = \lambda i_x \tag{a}$$

$$\lambda = \frac{A_w}{zF\rho} = \frac{55.85}{2*96500*7.87} = 3.6770 \times 10^{-5} \ \frac{V.cm^3}{A.s}$$

$$C_R = \left(3.6770 \times 10^{-5} \ \frac{V.cm^3}{A.s}\right)(60*60*24*365)(10)\, i_x$$

$$C_R = 11,596 i_x \ (in\, mm/yr)$$
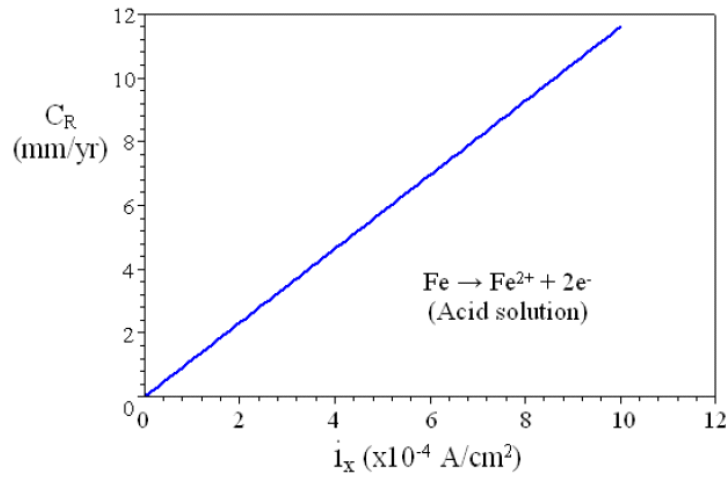
The slope of this plot represents the volume of Fe^{2+} ions per electric charge. Hence,

$$\frac{dC_R}{di_x} = \lambda = 3.6770 \times 10^{-5} \ \frac{cm^3}{A.s} \ (slope)$$

$$\frac{dC_R}{di_x} \simeq 0.038 \ \frac{mm^3}{A.s}$$

The upper and lower C_R values are

$$C_R = 11.60 \ mm/yr \ @E_{corr} \ (upper \ limit)$$

$$C_R = 1.16 \times 10^{-4} \ mm/yr \ @E_{Fe} \ (lower \ limit)$$

Therefore, corrosion can be minimized significantly as $i_x \to i_{Fe} = 10^{-8}$ A/cm^2. Upon decreasing i_x into the cathodic region at $E < E_{Fe}$, reduction of iron, $Fe^{2+} + 2e^- \to Fe$, occurs and $C_R = 0$. This electrochemical process leads to the principles of cathodic protection (CP) large structures. The theory of CP is dealt with in a later chapter.

(b) *Combining eq. (a) and (5.37a) gives*

$$C_R = \frac{i_a A_w}{zF\rho} = \lambda i_a$$

$$i_a = i_{corr} \exp\left(\frac{2.303\,(E_a - E_{corr})}{\beta_a}\right)$$

$$C_R = \lambda i_{corr} \exp\left(\frac{2.303\,(E_a - E_{corr})}{\beta_a}\right) \tag{b}$$

$$C_R = (11.60\ mm/yr) \exp\left(57.58 E_a + 14.39\right) \tag{c}$$

The non-linear corrosion rate profile is given by eq. (c) and it is depicted in the figure below.
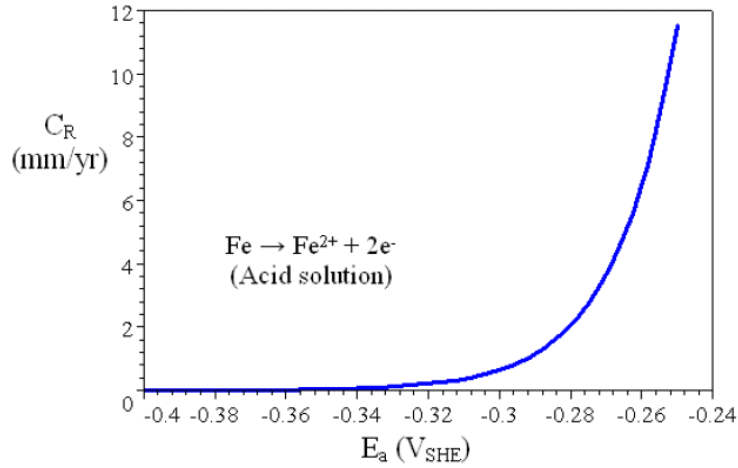
The upper and lower C_R values in this case are

$$C_R = 11.54\ mm/yr\ @E_{corr}\ (upper\ limit)$$

$$C_R = 1.15 \times 10^{-4}\ mm/yr\ @E_{Fe}\ (lower\ limit)$$

Basically, these results are the same as in part (a).

Chapter 6

MASS TRANSPORT BY DIFFUSION AND MIGRATION

6.1   PROBLEMS

6.1   Why convective mass transfer is independent of concentration gradient $\partial C/\partial x$ in eq. (6.2)?

Answer: *Because it arises due to fluid motion in which $\partial C/\partial x$ doe not play an important role. Only the bulk concentration and fluid velocity are the controlling parameters at a plane for convective motion.*

6.2   Use the information given in Example 6.3, part b, to determine the concentration rate in the x-direction at $1\ mm$ from the columns interface. Given data: $D = 10^{-5}\ cm^2/s$, $C_o = 10^{-4}\ mol/cm^3$ and $t = 10\ \sec$. [Solution: $\partial C/dt = 1.96x10^{-16}\ mol/cm^3.s$].

Solution:

From Example 6.2,

$$
\begin{aligned}
\frac{\partial C}{\partial x} &= -\frac{C_o}{\sqrt{4\pi Dt}}\exp\left(-\frac{x^2}{4Dt}\right)\\
\frac{\partial^2 C}{\partial x^2} &= \frac{xC_o}{4Dt\sqrt{\pi Dt}}\exp\left(-\frac{x^2}{4Dt}\right)
\end{aligned}
$$

Thus, Fick's second law becomes

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

$$\frac{\partial C}{\partial t} = \frac{xC_o}{4t\sqrt{\pi Dt}}\exp\left(-\frac{x^2}{4Dt}\right)$$

$$\frac{\partial C}{\partial t} = \frac{(0.1\ cm)\left(10^{-4}mol/cm^3\right)}{(4)\,(10\ s)\,\sqrt{(\pi)\,(10^{-5}\ cm^2/s)\,(10\ s)}}\exp\left[-\frac{(0.1\ cm)^2}{(4)\,(10^{-5}\ cm^2/s)\,(10\ s)}\right]$$

$$\frac{\partial C}{\partial t} = 1.96x10^{-16}\ \frac{mol}{cm^3.s}$$

6.3 What's the action of hydrogen on a steel blade exposed to an aqueous solution of hydrogen sulfide if the following reaction takes place $Fe + H_2S = FeS + 2H$? Assume that the steel blade gets damaged during service.

Answer: *Evolution of atomic hydrogen* (H) *on the steel surface may occur according to the reactions*

$$Fe \rightarrow F^{+2} + 2e$$
$$H_2S \rightarrow 2H^+ + S^{-2} + 2e$$
$$\overline{Fe + H_2S \rightarrow Fe^{+2} + S^{-2} + 2H^+ + 2e}$$

and

$$Fe^{+2} + S^{-2} + 2H^+ + 2e \rightarrow FeS + 2H$$
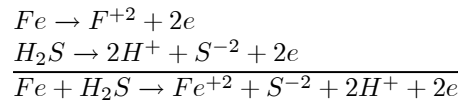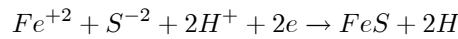
Atomic hydrogen readily diffuses into the steel (iron matrix) and locates there in voids, vacancies, and dislocations where $H + H \rightarrow H_2$ *occurs within the lattice. The formation of molecular hydrogen* (H_2) *in voids combine with other hydrogen molecules, building up a high pressure* (P) *that may exceed the yield strength* (σ_{ys}) *of the steel blade. If* $P > \sigma_{ys}$, *then blistering and fissures may occur and the steel strength and ductility decrease. This phenomenon is known as hydrogen embrittlement.*

6.4 An aerated acid solution containing $10^{-2}\ mol/l$ of dissolved oxygen (O_2) moves at $2x10^{-4}\ cm/s$ in a stainless steel pipe when a critical current density of $10^3\ \mu A/cm^2$ passivates the pipe. Calculate a) the thickness of the Helmholtz ionic structural layer (δ), b) the limiting current density (i_L) if the three modes of flux are equal in magnitude, and c) Will the pipe corrode under the current conditions? Why? or Why not? Data:

$$O_2 + 2H_2O + 4e^- = 4OH^- \qquad \text{(Cathode)}$$
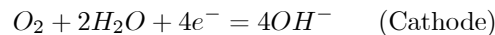
$D_{O_2} = 10^{-5}\ cm^2/s$	$T = 25^oC$	$F = 96,500\ A.s/mol$

Solutions:

a) *From eq. (6.1) along with* $C_b = 10^{-2} \ mol/l = 10^{-5} \ mol/cm^3$, *the molar fluxes are*

$$
\begin{aligned}
J(x,t)_c &= C_b v(x,t) = \left(10^{-5} \ mol/cm^3\right)\left(2x10^{-4} \ cm/s\right) \\
J(x,t)_c &= 2x10^{-9} \ \frac{mol}{cm^2.s} \\
J(x,t)_d &= 2x10^{-9} \ \frac{mol}{cm^2.s} = D\frac{\partial C}{\partial x} = \frac{DC_b}{\delta} \\
J(x,t)_m &= 2x10^{-9} \ \frac{mol}{cm^2.s} = \frac{zFDC_b}{RT}\frac{d\phi}{dx}
\end{aligned}
$$

Thus, the total molar flux becomes

$$
\begin{aligned}
J(x,t) &= J(x,t)_d + J(x,t)_m + J(x,t)_c \\
J(x,t) &= 3J(x,t)_c \\
J(x,t) &= 3C_b v(x,t) = 6x10^{-9} \ \frac{mol}{cm^2.s}
\end{aligned}
$$

But,

$$
\begin{aligned}
\frac{DC_b}{\delta} &= C_b v(x,t) = J(x,t)_c \\
\delta &= \frac{D}{v(x,t)} = \frac{10^{-5} \ cm^2/s}{2x10^{-4} \ cm/s} \\
\delta &= 0.05 \ cm = 0.5 \ mm
\end{aligned}
$$

b) *From eq. (6.8)*

$$
\begin{aligned}
i &= zFJ(x,t) \\
i &= (4)\left(96,500 \ \frac{A.s}{mol}\right)\left(6x10^{-9} \ \frac{mol}{cm^2.s}\right) \\
i &= i_L = 2.32x10^{-3} \ \frac{A}{cm^2} = 2.32x10^3 \ \frac{\mu A}{cm^2}
\end{aligned}
$$

c) *Corrosion will not occur because* $i_L = 2.32x10^3 \ \mu A/cm^2 > i_{crit} = 10^3 \ \mu A/cm^2$.

6.5 a) Determine the oxygen concentration for Problem 6.4 that will promote corrosion of the stainless steel pipe. b) How long will it take for corrosion to occur?

Solutions:

a) *For a diffusional process only, From eq. (6.9a) yields along with $\partial C/\partial x \simeq DC_b/\delta$ and $i = i_c$,*

$$C_b = \frac{i_c\delta}{zFD} = \frac{\left(10^{-3}\ A/cm^2\right)(0.05\ cm)}{(4)\,(96,500\ A.s/mol)\,(10^{-5}\ cm^2/s)}$$

$$C_b = 1.30x10^{-2}\ mol/l = 1.30x10^{-5}\ mol/cm^3$$

This result indicates that approximately $100\%\left(1.30x10^{-2} - 10^{-2}\right)/1.30x10^{-2} = 23\%$ *increase in oxygen content will cause corrosion.*

b) *From* eq. (6.52),

$$i_c = \frac{zFC_b}{\sqrt{\pi Dt}}$$

$$t = \frac{D}{\pi}\left[\frac{zFC_b}{i_c}\right]^2$$

$$t = \left(\frac{10^{-5}\ cm^2/s}{\pi}\right)\left[\frac{(4)\,(96,500\ A.s/mol)\left(1.30x10^{-5}\ mol/cm^3\right)}{10^{-3}\ A/cm^2}\right]^2$$

$$t = 80.15\ s = 1.34\ min.$$

6.6 Use the given data to calculate a) the diffusivity of copper ions in a cathodic process at 25^oC and b) the valence z. The original concentration in an acidic solution is 60 g/l.

t (sec)	i $\left(A/cm^2\right)$	$\partial C/\partial x$ $\left(mol/cm^4\right)$
0	0	0
5	0.1455	0.07532
10	0.1029	0.05326
15	0.0840	0.04349
20	0.0728	0.03766

Solution:

$C_b = 60\ g/l = (60g/l)\,(63.55\ g/mol) = 0.9443\ mol/l$
$C_b = 9.443x10^{-4}\ mol/l$
a) *Linear regression analysis:From* eq. (6.48),

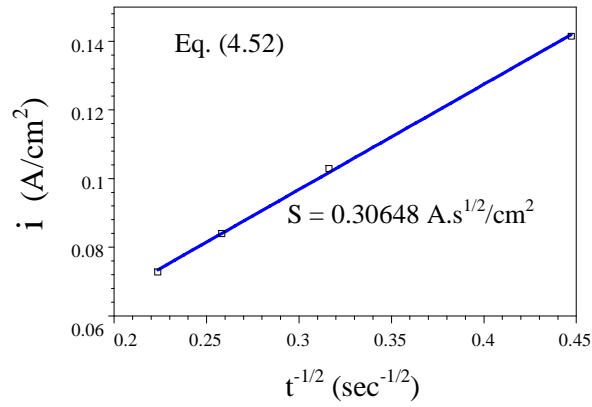$$\frac{\partial C}{\partial x} = 1.801\,5 \times 10^{-6}\ \frac{mol}{cm^4} + \left(0.16842\ \frac{mol.s^{1/2}}{cm^4}\right)t^{-1/2}$$
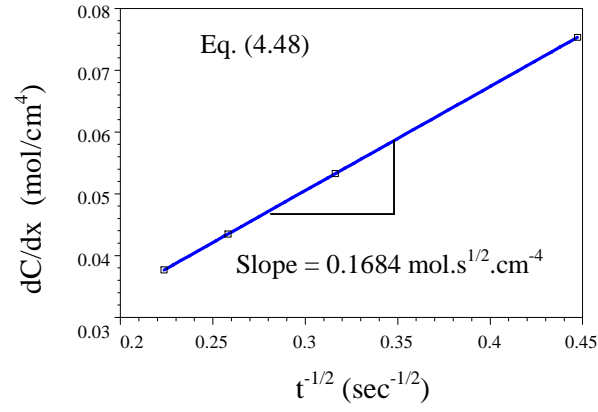
From eq. (6.48),

$$\frac{\partial C}{\partial x} = \frac{C_b}{\sqrt{\pi D t}} = \left(\frac{C_b}{\sqrt{\pi D}}\right) t^{-1/2}$$

$$S = \frac{C_b}{\sqrt{\pi D}} = 0.16842 \ \frac{mol.s^{1/2}}{cm^4}$$

$$D = \frac{1}{\pi}\left(\frac{C_b}{S}\right)^2 = \frac{1}{\pi}\left(\frac{9.443x10^{-4}mol/cm^3}{0.16842 \ mol.s^{1/2}/cm^4}\right)^2$$

$$D = 10^{-5} \ cm^2/s$$

b) *Polynomial fit:*

$$i = 4.8903 \times 10^{-3} \ A/cm^2 + \left(0.30648 \ A.s^{1/2}/cm^2\right) t^{-1/2}$$

From eq. (6.52),

$$i = \frac{zFDC_b}{\sqrt{\pi D t}}$$

$$i = \left(\frac{zFDC_b}{\sqrt{\pi D}}\right) t^{-1/2}$$

$$S = \frac{zFDC_b}{\sqrt{\pi D}} = 0.30648 \ A.s^{1/2}/cm^2$$

$$z = \frac{S\sqrt{\pi/D}}{FC_b} = \frac{\left(0.30648 \ A.s^{1/2}/cm^2\right)\sqrt{\pi/10^{-5} \ cm^2/s}}{(96,500 \ A.s/mol)\left(9.443x10^{-4}mol/cm^3\right)}$$

$$z = 2$$

6.7 It is desired to reduce copper, $Cu^{+2} + 2e^- = Cu$, at 35^oC from an electrolyte containing $60 \ g/l$ of Cu^{+2} ions. Calculate a) the total molar flux that arises from equal amounts of diffusion and migration mass transfer under steady-state conditions, b) the gradients dc/dx, $d\phi/dx$, and $d\mu/dx$, and c) approximate the thickness of the diffusion layer at the cathode electrode surface. Operate the electrowinning cell for 10 minutes and let the diffusivity for Cu^{+2} ions be $10^{-5} \ cm^2/s$.

Solutions:

$C_b = 60 \ g/l = (60 \ g/l)(63.55 \ g/nol)$	$t = 10 \ \min = 600 \ sec$
$C_b = 0.944 \ mol/l$	$z = 2$
$C_b = 9.44x10^{-4} \ mol/cm^3$	$F = 96,500 \ A.s/mol$
$D = 10^{-5} \ cm^2/s$	$k = 1.38x10^{-23} \ J/^oK$

a) *From* eq. (6.52),

$$i = \frac{zFDC_b}{\sqrt{\pi Dt}} = zFC_b\sqrt{\frac{D}{\pi t}}$$

$$i = (2)(96,500 A.s/mol)(9.44x10^{-4} \ mol/cm^3)\sqrt{\frac{(10^{-5} \ cm^2/s)}{(\pi)(600 \ sec)}}$$

$$i = 1.33x10^{-2} \ A/cm^2$$

From eq. (6.8),

$$i = zFJ$$

$$J = \frac{i}{zF} = \frac{1.33x10^{-2} \ A/cm^2}{(2)(96,500 \ A.s/mol)}$$

$$J = 6.88x10^{-8} \ \frac{mol}{cm^2.s}$$

b) *Both diffusion and migration fluxes are equal. Thus,*

$$J = J_d + J_m$$

$$J_d = J_m = J/2 = 3.44x10^{-8} \ \frac{mol}{cm^2.s}$$

From eq. (6.48),

$$\frac{\partial C}{\partial x}\bigg|_{x=0} = \frac{C_b}{\sqrt{\pi Dt}} = \frac{9.44x10^{-4} \ mol/cm^3}{\sqrt{(\pi)(10^{-5} \ cm^2/s)(600 \ sec)}}$$

$$\frac{\partial C}{\partial x}\bigg|_{x=0} = 3.88x10^{-3} \ \frac{moil}{cm^4}$$

From eq. (6.15), *the ionic mobility is*

$$B = \frac{D}{kT} = \frac{10^{-5} \ cm^2/s}{(1.38x10^{-23} \ J/^oK)(308^oK)}$$

$$B = 2.35x10^{15} \ \frac{cm^2}{J.s} = 2.35x10^{15} \ \frac{V.cm^2}{C.s}$$

Now, using eq. (6.12) *yields*

$$\frac{d\phi}{dx} = -\frac{J_m}{zq_eC_bB}$$

$$\frac{d\phi}{dx} = -\frac{3.44x10^{-8}\frac{mol}{cm^2.s}}{(2)(1.602x10^{-19} \ C)(9.44x10^{-4}\frac{mol}{cm^3})(2.35x10^{15} \ \frac{V.cm^2}{C.s})}$$

$$\frac{d\phi}{dx} = -4.83x10^{-2} \ V/cm$$

From eq. (6.11),

$$\frac{d\mu}{dx} = zq_e \frac{d\phi}{dx}$$

$$\frac{d\mu}{dx} = (2) \left(1.602x10^{-19} \ J/V \right) \left(-4.83x10^{-2} \ V/cm \right)$$

$$\frac{d\mu}{dx} = -1.55x10^{-20} \ J/cm$$

c) *From* eq. (6.53),

$$\delta = \sqrt{\pi Dt}$$

$$\delta = \sqrt{(\pi) \left(10^{-5} \ cm^2/s \right) (600 \ s)}$$

$$\delta = 0.137 \ cm = 1.37 \ mm$$

6.8 Show that $J_{x=o} = DC_o/\delta$.

Solution:

Using eq. (6.40) *for activation polarization* $(C_o > C_b = C_\infty)$ *yields*

$$C_x = C_o - (C_o - C_b) \, \text{erf} \, (y) \qquad (4.40)$$

$$y = \frac{x}{\sqrt{4Dt}} \qquad dy = \frac{dx}{2\sqrt{Dt}} \qquad (a)$$

$$y^2 = \frac{x^2}{4Dt} \qquad (b)$$

$$\text{erf} \, (y) = \frac{2}{\sqrt{\pi}} \int_o^y \exp\left(-y^2 \right) dy \qquad (c)$$

Rearranging eq. (6.40) *along with* $C = C_x$ *and* $C_o > C_b = C_\infty$ *gives*

$$C = C_o - C_o \left[\frac{2}{\sqrt{\pi}} \int_o^y \exp\left(-y^2 \right) dy \right]$$

$$C = C_o - C_o \left[\frac{2}{\sqrt{\pi}} \int_o^y \exp\left(-\frac{x^2}{4Dt} \right) \frac{dx}{2\sqrt{Dt}} \right]$$

$$C = C_o - \frac{C_o}{\sqrt{\pi Dt}} \left[\int_o^y \exp\left(-\frac{x^2}{4Dt} \right) dx \right] \qquad (d)$$

Thus,

$$\frac{\partial C}{\partial x} = -\frac{C_o}{\sqrt{\pi Dt}} \frac{\partial}{\partial x} \left[\int_o^y \exp\left(-\frac{x^2}{4Dt} \right) dx \right]$$

$$\frac{\partial C}{\partial x} = -\frac{C_o}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt} \right)$$

$$\left. \frac{\partial C}{\partial x} \right|_{x=o} = -\frac{C_o}{\sqrt{\pi Dt}} \qquad (e)$$

Combining eqs. (6.3) and (e) yields

$$J_{x=o} = -D \left. \frac{\partial C}{\partial x} \right|_{x=o}$$

$$J_{x=o} = \frac{DC_o}{\sqrt{\pi D t}} = \frac{DC_o}{\delta} \qquad\qquad ((4.51))$$

6.9 Show that $dC/dx = C_b/\sqrt{\pi D t}$.

Solution:

Using eq. (6.38) for activation polarization $(C_b = C_\infty \gg C_o)$ *yields*

$$C_x = C_o + (C_b - C_o)\,\mathrm{erf}\,(y) \qquad\qquad (4.38)$$
$$C_x = C_o + C_b\,\mathrm{erf}\,(y) \qquad\qquad (a)$$
$$y = \frac{x}{\sqrt{4Dt}} \qquad dy = \frac{dx}{2\sqrt{Dt}} \qquad\qquad (b)$$
$$y^2 = \frac{x^2}{4Dt} \qquad\qquad (c)$$
$$\mathrm{erf}\,(y) = \frac{2}{\sqrt{\pi}} \int_o^y \exp\left(-y^2\right) dy \qquad\qquad (d)$$

Rearranging eq. (6.40) along with $C = C_x$ *gives*

$$C = C_o + C_b \left[\frac{2}{\sqrt{\pi}} \int_o^y \exp\left(-y^2\right) dy \right]$$
$$C = C_o + C_b \left[\frac{2}{\sqrt{\pi}} \int_o^y \exp\left(-\frac{x^2}{4Dt}\right) \frac{dx}{2\sqrt{Dt}} \right]$$
$$C = C_o + \frac{C_b}{\sqrt{\pi D t}} \left[\int_o^y \exp\left(-\frac{x^2}{4Dt}\right) dx \right] \qquad\qquad (e)$$

Thus,

$$\frac{\partial C}{\partial x} = \frac{C_b}{\sqrt{\pi D t}} \frac{\partial}{\partial x} \left[\int_o^y \exp\left(-\frac{x^2}{4Dt}\right) dx \right]$$
$$\frac{\partial C}{\partial x} = \frac{C_b}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right)$$
$$\left. \frac{\partial C}{\partial x} \right|_{x=o} = \frac{C_b}{\sqrt{\pi D t}} \qquad\qquad (e)$$

6.10 Prove that the diffusivity D is constant in the Fick's second law, eq. (6.17).

Solution:

From eq. (6.39),

$$\frac{C_x - C_o}{C_b - C_o} = \text{erf}(y)$$

$$\frac{C_x - C_o}{C_b - C_o} = \text{erf}\left(\frac{x}{\sqrt{4Dt}}\right)$$

For fixed values of distance x, time t, temperature T and concentration C_x,

$$\frac{C_x - C_o}{C_b - C_o} = \text{Constant} = \text{erf}\left(\frac{x}{\sqrt{4Dt}}\right)$$

Therefore, the diffusivity is

$$D = D_o \exp\left(-\frac{E^*}{RT}\right) = \text{Constant}$$

$$D \neq f(C_x)$$

6.11 Assume that the total molar flux of a specie j is due to diffusion and convection. The convective force acting on the specie is $F_x = -(1/N_A)(d\Delta G/dx)$, where N_A is Avogadro's number and $d\Delta G/dx$ is the molar free energy gradient. Recall that the volume fraction is equals to the mole fraction divided by molar concentration; that is, $V = X/C$. Based on this information, show that

$$\frac{dC}{dx} = C\left[\frac{d\ln(C/C_o)}{dx}\right]$$

where $J_d = J_c$, $K = C/C_o < 1$ and $C_o = $ Constant.

Solution:

Combining eqs. (6.5) and (6.13) yields

$$J_c = Cv = CBF_x$$

$$J_c = -\frac{CB}{N_A}\frac{d\Delta G}{dx}$$

Thermodynamically, the free energy change is defined by eq. (2.31a)

$$\Delta G = \Delta G^o + RT\ln(K)$$

$$\Delta G = \Delta G^o + RT\ln(C/C_o)$$

$$\frac{d\Delta G}{dx} = RT\frac{d[\ln(K)]}{dx}$$

where K is the rate constant. Thus,

$$J_c = -\frac{CBRT}{N_A}\frac{d\left[\ln\left(C/C_o\right)\right]}{dx}$$

$$J_c = -CkBT\left[\frac{d\left[\ln\left(C/C_o\right)\right]}{dx}\right]$$

since $k = R/N_A =$ Boltzmann constant. Fick's first law gives

$$J_d = -D\frac{\partial C}{\partial x}$$

If $J_d = J_c$, then

$$-D\frac{\partial C}{\partial x} = -CkBT\left[\frac{d\left[\ln\left(C/C_o\right)\right]}{dx}\right]$$

$$kBT\frac{\partial C}{\partial x} = CkBT\left[\frac{d\left[\ln\left(C/C_o\right)\right]}{dx}\right]$$

$$\frac{\partial C}{\partial x} = C\left[\frac{d\left[\ln\left(C/C_o\right)\right]}{dx}\right]$$

since $D = kBT$ as in eq. (6.15). *This concludes the solution of the problem.*

6.12 Use the information given in Problem 6.11 to show that

$$\frac{d\Delta G}{dx} = \frac{RT}{C}\frac{dC}{C}$$

Solution:

Thermodynamically, the free energy change is defined by eq. (2.31a)

$$\Delta G = \Delta G^o + RT\ln\left(K\right)$$

$$\Delta G = \Delta G^o + RT\ln\left(C/C_o\right)$$

$$\frac{d\Delta G}{dx} = RT\frac{d\ln\left(C/C_o\right)}{dx}$$

But,

$$\frac{1}{C}\frac{dC}{dx} = \frac{d\ln\left(C/C_o\right)}{dx}$$

Then,

$$\frac{d\Delta G}{dx} = \frac{RT}{C}\frac{dC}{dx}$$

6.13 Use the information given in Problem 6.12 to show that

$$v_x = -\frac{D}{C}\frac{dC}{dx}$$

Solution:

From eqs. (6.13) *and Problem* 6.11,

$$v = BF_x \tag{4.13}$$
$$F_x = -\frac{1}{N_A}\frac{d\Delta G}{dx}$$

Thermodynamically, the free energy change is defined by eq. (2.31a)

$$\Delta G = \Delta G^o + RT \ln (K)$$
$$\Delta G = \Delta G^o + RT \ln (C/C_o)$$
$$\frac{d\Delta G}{dx} = RT\frac{d\ln (C/C_o)}{dx}$$

But,

$$\frac{1}{C}\frac{dC}{dx} = \frac{d\ln (C/C_o)}{dx}$$

Then,

$$\frac{d\Delta G}{dx} = \frac{RT}{C}\frac{dC}{dx}$$

Thus, eq. (6.13) *yields the drift velocity as*

$$v = -\frac{BkT}{C}\frac{dC}{dx}$$
$$v = -\frac{D}{C}\frac{dC}{dx}$$

where $D = BkT$.

6.14 If the migration flux is neglected in eq. (6.2), approximate the total flux at low and high temperatures. Assume that $C_x \gg C_o$ at a distance x from an electrode surface.

Solution:

$$J = -D\frac{dC}{dx} + Cv$$
$$J = -D\frac{C_o - C}{x} + Cv$$

If $C \gg C_o$, then

$$J = -\frac{DC}{x} + Cv$$

In addition,

$$D = D_o \exp\left(-\frac{E^*}{RT}\right)$$

and

$$J = -\frac{CD_o}{x} \exp\left(-\frac{E^*}{RT}\right) + Cv$$

Mathematically,

- *@ If $T \to 0$, then $D \to 0$ and $J = J_c \simeq Cv$*

- *@ If $T \to \infty$, then $D \to D_o$ and*

$$J \simeq -\frac{CD_o}{x} + Cv$$

This analysis indicates that the diffusivity D and the molar flux J increase with increasing temperature.

6.15 Consider the concentration plane shown below. This is a transient electrochemical system having finite dimensions. Derive a solution for Fick's second law, $\partial C/\partial t = D\partial^2 C/\partial x^2$, based on this information
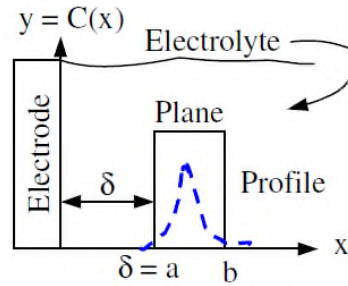
Solution:

Following the analytical procedure in Appendix A yields

$$y = \frac{x}{2\sqrt{Dt}} \qquad y_1 = \frac{a - x}{2\sqrt{Dt}} \qquad y_2 = \frac{b - x}{2\sqrt{Dt}}$$

Start with eq. (A6) and (A8):

$$\int_o^{C_b} dC = B \int_{-\infty}^{\infty} \exp\left(-y^2\right) dy = \sqrt{\pi}B$$
$$C_b = \sqrt{\pi}B$$
$$B = \frac{C_b}{\sqrt{\pi}}$$

Then,

$$
\int_o^C dC = \frac{C_b}{\sqrt{\pi}} \int_{y_1}^{y_2} \exp\left(-y^2\right) dy
$$

$$
\int_o^C dC = \frac{C_b}{2} \left[\frac{2}{\sqrt{\pi}} \int_o^{y_2} \exp\left(-y^2\right) dy - \frac{2}{\sqrt{\pi}} \int_o^{y_2} \exp\left(-y^2\right) dy \right]
$$

$$
\frac{C}{C_b} = \frac{1}{2} \left[\mathrm{erf}\left(y_2\right) - \mathrm{erf}\left(y_1\right) \right]
$$

6.16 Derive Fick's second law if the volume element in Figure 6.2 has a unit cross-sectional area and a thickness x.

Solution:

$$
J_{x,in} = D \left(\frac{\partial C}{\partial x} \right)_x
$$

$$
J_{x,out} = -D \left(\frac{\partial C}{\partial x} \right)_{x+dx} = -D \left(\frac{\partial C}{\partial x} \right)_x - D \left(\frac{\partial C}{\partial x} \right)_{dx}
$$

The concentration rate is

$$
\frac{\partial C}{\partial t} = -\frac{\partial J_x}{\partial x} = -\frac{\partial J_{x,in}}{\partial x} - \frac{\partial J_{x,out}}{\partial x}
$$

$$
\frac{\partial C}{\partial t} = -D \left(\frac{\partial^2 C}{\partial x^2} \right)_x + D \left(\frac{\partial^2 C}{\partial x^2} \right)_x + D \left(\frac{\partial^2 C}{\partial x^2} \right)_{dx}
$$

$$
\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} \right)_{dx}
$$

$$
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}
$$

6.17 What does Fick's first law mean in terms of atoms or ions of a single phase?

Answer: *Fick's first law, $J_x = D \left(\frac{\partial C}{\partial x} \right)$, means that atoms or ions diffuse from high to low concentration regions.*

6.18 What will Fick's first law mean if D does not vary with x or C?

Answer: *Fick's first law will mean that $J_x = D \frac{\partial C}{\partial x}$ becomes a linear relationship under steady-state condition $\left(\frac{\partial C}{\partial t} = 0 \right)$ and hat atoms or ions diffuse from high to low concentration regions.*

6.19 Derive Fick's second law if the volume element in Figure 6.2 has a unit cross-sectional area and the diffusing plane is located between x and $x + dx$, where J_x is the entering molar flux at x and J_{x+dx} is that leaving at $x + dx$.

Solution:

Using Fick's first law and the continuity equation yields

$$\frac{\partial C}{\partial t} = -\frac{\partial J_x}{\partial x}$$

$$J_x = -D\frac{\partial C}{\partial x}$$

$$\frac{\partial C}{\partial t} = \frac{1}{\partial x}\left[D\frac{\partial C}{\partial x}\right]$$

$$\frac{\partial C}{\partial t} = \frac{\partial D}{\partial x}\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2}$$

If D is constant, then Fick's second law becomes

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

6.20 Find an expression for x when

$$\frac{C_x - C_b}{C_o - C_b} = 0.5205 = \text{erf}\left(\frac{x}{\sqrt{4Dt}}\right)$$

Solution:

$$\frac{C_x - C_b}{C_o - C_b} = 0.5205 = \text{erf}\left(\frac{x}{\sqrt{4Dt}}\right)$$

$$\frac{C_x - C_b}{C_o - C_b} = 0.5205 = \text{erf}\,(y)$$

$$0.5205 = \text{erf}\,(y)$$

From Table 6.2,

$$y = \frac{x}{\sqrt{4Dt}}$$

$$\frac{1}{2} = \frac{x}{2\sqrt{Dt}}$$

$$x = \sqrt{Dt}$$

6.21 Derive eq. (6.85).

Solution:

Using eq. *(6.82) for oxidation yields*

$$i = zFD \left[\frac{dC_x}{dx} + \frac{C_x}{RT} \frac{d\phi}{dx} \right]$$

$$\frac{di}{dx} = zFD \left[\frac{d^2C}{dx^2} + \frac{C}{RT} \frac{d^2\phi}{dx^2} + \frac{1}{RT} \frac{dC}{dx} \frac{d\phi}{dx} \right] = 0 \tag{a}$$

From eq. *(6.48) along with constant D at fixed time t and with $C = C_b =$ constant at $x \to \infty$ in the bulk electrolyte,*

$$\frac{dC}{dx} = \frac{C_b}{\sqrt{\pi Dt}} \tag{b}$$

$$\frac{d^2C}{dx^2} = 0 \tag{c}$$

Inserting eqs. (b) and (c) into (a) yields

$$\frac{d^2\phi}{dx^2} + \frac{1}{\sqrt{\pi Dt}} \frac{d\phi}{dx} = 0 \tag{4.62}$$

6.22 Show that $d\phi/dx = -7\phi_o/\left(19\sqrt{\pi Dt}\right)$ in a coupled diffusion and migration mass transfer. let $x = \sqrt{\pi Dt}$.

Solution:

Using eq. *(6.64) yields*

$$\phi = \phi_o \exp\left(-\frac{x}{\sqrt{\pi Dt}}\right)$$

$$\frac{d\phi}{dx} = -\frac{\phi_o}{\sqrt{\pi Dt}} \exp\left(-\frac{x}{\sqrt{\pi Dt}}\right)$$

$$\frac{d\phi}{dx} = -\frac{\phi_o}{\sqrt{\pi Dt}} \exp\left(-\frac{\sqrt{\pi Dt}}{\sqrt{\pi Dt}}\right)$$

$$\frac{d\phi}{dx} = -\frac{\phi_o}{\sqrt{\pi Dt}} \exp(-1)$$

$$\frac{d\phi}{dx} = -\frac{0.368\phi_o}{\sqrt{\pi Dt}}$$

$$\frac{d\phi}{dx} = -\frac{7\phi_o}{19\sqrt{\pi Dt}}$$

6.23 For activation polarization, the concentration gradient is given by eq. (6.50). If $C_o \gg C_b$, then show that

$$\frac{C}{C_o} = \frac{1}{\sqrt{4\pi Dt}} \left(\frac{x^3}{12Dt} - x \right)$$

Solution:

From eq. (6.49) along with $C_o \gg C_b$,

$$\frac{dC}{dx} = -\frac{C_o}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt} \right)$$

a) Taylor's series: Letting $y = x^2/(4Dt)$ and expanding the exponential function, $\exp(-y) = \sum (-y)^k /k! \simeq 1 - y$, yields

$$\frac{dC}{dx} = -\frac{C_o}{\sqrt{4\pi Dt}} (1 - y)$$

$$\frac{dC}{dx} = -\frac{C_o}{\sqrt{4\pi Dt}} \left(1 - \frac{x^2}{4Dt} \right)$$

$$\frac{dC}{dx} = \frac{C_o}{\sqrt{4\pi Dt}} \left(\frac{x^2}{4Dt} - 1 \right)$$

b) Using the first three terms of McClaurin series yields

$$f(x) = f(0) + \frac{f'(0)}{1!} x + \frac{f''(0)}{2!} x^2 + \frac{f'''(0)}{3!} x^3 + \dots.$$

$$f(x) = \exp\left(-\frac{x^2}{4Dt} \right)$$

$$f(x = 0) = \exp\left(-\frac{x^2}{4Dt} \right)_{x=0} = 1$$

$$f'(x = 0) = -\frac{2x}{4Dt} \exp\left(-\frac{x^2}{4Dt} \right)_{x=0} = 0$$

$$f''(x = 0) = -\frac{1}{2Dt} \exp\left(-\frac{x^2}{4Dt} \right)_{x=0} + \frac{x^2}{4D^2t^2} \exp\left(-\frac{x^2}{4Dt} \right)_{x=0}$$

$$f''(x = 0) = -\frac{1}{2Dt}$$

$$f(x) = \exp\left(-\frac{x^2}{4Dt} \right) = 1 - \frac{x^2}{4Dt}$$

Then,

$$\frac{dC}{C_o} = \frac{1}{\sqrt{4\pi Dt}} \left(\frac{x^2}{4Dt} - 1 \right) dx$$

$$\frac{1}{C_o} \int_o^C dC = \frac{1}{\sqrt{4\pi Dt}} \int_o^x \left(\frac{x^2}{4Dt} - 1 \right) dx$$

$$\frac{C}{C_o} = \frac{1}{\sqrt{4\pi Dt}} \left(\frac{x^3}{12Dt} - x \right)$$

6.24 Derive eq. (5.122) by converting eq. (3.29) into chemical potential (μ) if only one ion participates in a reaction. The reaction constant is defined by $K_r = \gamma C$, where γ is the activity coefficient and C is the concentration. Let the molar diffusion and migration be equal and $J_c = 0$ in eq. (6.10).

Solution:

$$\mu = \mu^o + kT \ln (K_r) = \mu^o + kT \ln (\gamma C)$$
$$\mu = \mu^o + kT \ln (\gamma) + \ln (C)$$
$$\frac{d\mu}{dC} = \frac{kT}{C}$$

Let

$$\frac{d\mu}{dx} = \frac{d\mu}{dC}\frac{dC}{dx} = \frac{kT}{C}\frac{dC}{dx}$$

and

$$J_d = J_m$$
$$-D\frac{dC}{dx} = -CB\frac{d\mu}{dx} = -BkT\frac{dC}{dx}$$
$$D = BkT$$

6.25 Follow the statement given in Example 6.3 for determining the average concentration as the starting point in this problem. Let $C_{o,1}$ and $C_{o,2}$ be the original concentrations of columns 1 and 2, respectively.
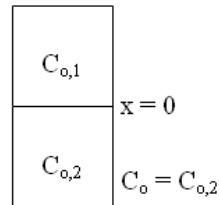
Solution:

Start with

$$\frac{C_x - C}{C_{o,1} - C} = \text{erf}\left(\frac{x}{\sqrt{\pi Dt}}\right)$$

Average concentration:

$$C = \frac{C_{o,1} + C_{o,2}}{2} = \frac{C_o}{2}$$
$$C = \frac{C_o}{2}$$

Thus,

$$\frac{C_x}{C_o} = \frac{1}{2}\left[\text{erf}\left(\frac{x}{\sqrt{\pi Dt}}\right)\right]$$

$$\frac{C_x}{C_o} = \frac{1}{2} \quad @ \ x = 0$$

The rest of the problem is worked out in Example 6.3.

6.26 This problem requires the determination of the total molar flux and current density profiles due to diffusion, migration and convection for the reduction of nickel from an electrolyte containing $8x10^{-4}$ mol/cm^3 of Ni^{+2} cations. The electrochemical cell has a continuos and direct fluid flow system of 20 cm/s at 35^oC. The diffusivity of Ni^{+2} cations is $D = 1.44 \times 10^{-5}$ cm^2/s. a) Use $0 \le t \le 100$ seconds for $J_x = f(t, x = 0)$ at the electrode surface and b) $0 \le x \le 10$ centimeters for $J_x = f(x, t = 10)$, and c) analyze the resultant profiles very succinctly and determine which molar flux dominates in this hypothetical reduction process for Ni^{+2} cations from solution. Can this process achieve a steady-state?

Solution:

$Ni^{+2} + 2e = Ni \qquad z = 2 \qquad F = 96,500 \ A.s/mol$
$C_b = 8 \times x10^{-4} \, \text{mol}/\,\text{cm}^3$
$v_b = 20 \ \text{cm}/\,\text{s}$
$D = 1.44 \times 10^{-5} \ \text{cm}^2/\,\text{s}$

Electrode Surface: Using eqs. (6.5), (6.64a), and (6.54b) yields the molar fluxes on the electrode surface $(x = 0)$

$$J_c = C_b v_b = 0.002 \ mol/cm^2.s$$

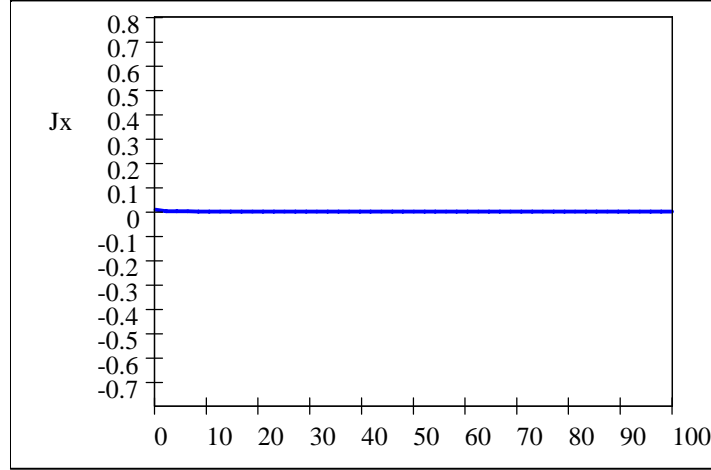$$J_m = (DC_b)/\sqrt{\pi Dt} = \left(1.712\,8 \times 10^{-3}\right)/\sqrt{t}$$

$$J_d = (DC_b)/\sqrt{\pi Dt} = \left(1.712\,8 \times 10^{-3}\right)/\sqrt{t}$$

$$J_x = J_d + J_m + J_c$$

$$J_x = \frac{(2)\left(1.712\,8 \times 10^{-3}\right)}{\sqrt{t}} + 0.002$$

$$J_x = \frac{3.4256 \times 10^{-3}}{\sqrt{t}} + 0.002$$

where t is in seconds and J_x in $mol.cm^{-2}s^{-1}$. Thus, the J_x vs. t profile is shown below.

Problem 4.26a

This profile indicates that $J_x \to -\infty$ as $t \to 0$ and this is a transient process. However $J_x \to 0$ as $t \to \infty$ which is the condition for a steady-state process. These theoretical analysis can further be confirmed by letting $t = 10$ seconds and vary the distance x from the electrode surface. Hence,

Fixed Time: Using eqs. (6.5), (6.64), (6.4) and (6.3) yields
$J_c = C_b v_b = 0.002 \ mol/cm^2.s$

$t = 10\,\mathrm{s}$
$\phi = \phi_o \exp\left(-x/\delta\right) = RT\left(zF\right)^{-1}\exp\left(-x/\sqrt{\pi Dt}\right)$
$d\phi/dx = RT\left(zF\sqrt{\pi Dt}\right)^{-1}\exp\left(-x/\sqrt{\pi Dt}\right)$
$J_m = \left(DC_b\right)\left(RT\right)^{-1}d\phi/dx$
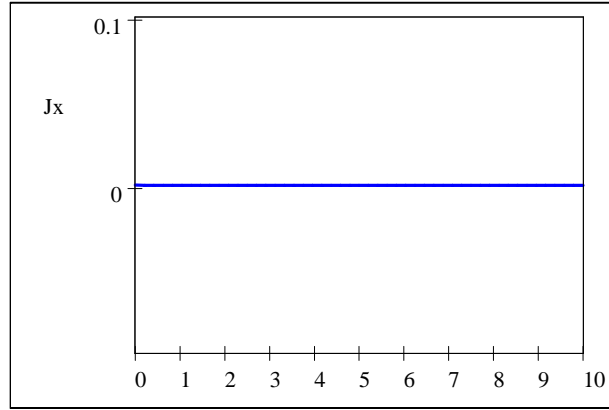$J_m = \left(DC_b\right)\left(\sqrt{\pi Dt}\right)^{-1}\exp\left(-x/\sqrt{\pi Dt}\right)$
$J_m = 5.416\,2 \times 10^{-7}\exp\left(-47.016x\right)$

$J_d = -D\partial C_x/\partial x = DC_b\left(\sqrt{31.416D}\right)^{-1}\exp\left(-x^2\left(40D\right)^{-1}\right)$
$J_d = \left(5.416\,2 \times 10^{-7}\right)\exp\left(-1736.1x^2\right)$
$J_x = J_d + J_m + J_c$

$$J_x = \left(5.416\,2 \times 10^{-7}\right) \exp\left(-1736.1x^2\right) + \left(5.416\,2 \times 10^{-7}\right) \exp\left(-47.016x\right) + 0.002$$


This confirms that a steady-state is achieved at $t \geq 10$ seconds. It can also be concluded that the convective molar flux controls the electrodeposition since $J_x \approx J_c \approx 0.002$ $mol/cm^2.s$. Therefore, an effective electrolyte flow system is important in electrodeposition. Similarly profiles result for the current density.

$$J_x = \frac{(2)\left(1.712\,8 \times 10^{-3}\right)}{\sqrt{t}} + 0.002 = \frac{3.425\,6 \times 10^{-3}}{\sqrt{t}} + 0.002$$

Using eq. (6.9) yield i in A/cm^2 and time t in seconds

$$i = zFJ_x = (2)(96500)\left(\frac{3.425\,6 \times 10^{-3}}{\sqrt{t}} + 0.002\right)$$
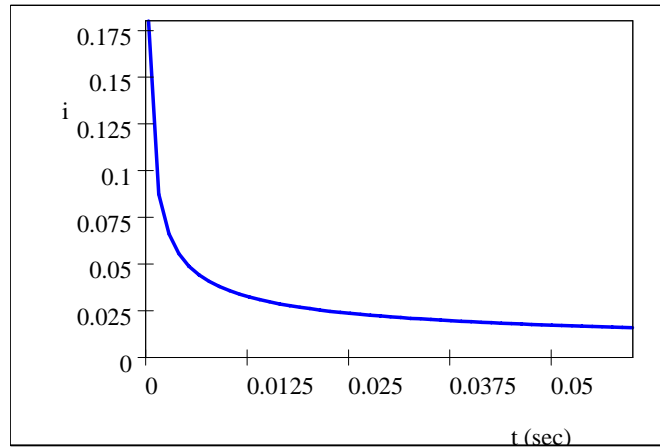
This profile indicates that the current density in A/cm^2 is sufficiently high, but it rapidly decreases as the electrochemical process progresses. For instance, at $t = 0.01$ sec the current density is $i = 3.63x10^{-2}$ A/cm^2. In addition,

$$i = zFJ_x$$
$$i = (2)(96500)\left(\begin{array}{c}\left(5.416\,2\times 10^{-7}\right)\exp\left(-1736.1x^2\right)\\ +\left(5.416\,2\times 10^{-7}\right)\exp\left(-47.016x\right)+0.002\end{array}\right)$$
$$i = 0.104\,53\exp\left(-1736.1x^2\right)+0.104\,53\exp\left(-47.016x\right)+386.0$$
$$i = 386\ A/cm^2$$
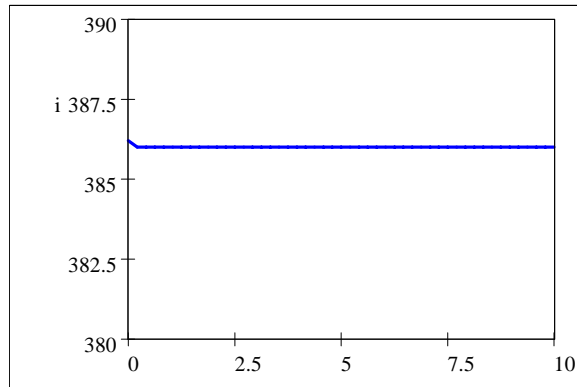
6.27 **(a)** Derive an expression for the concentration in g/l as a function of temperature T and distance x from an oxidizing pure copper electrode in an electrolyte under an electrostatic field. Use the chemical potential gradient, $d\mu/dx = -(zF)\,d\phi/dx$ with an electric potential decay, $\phi_x = \phi_o \exp\left(-\lambda x\right)$ Let

the free energy change be defined as $\Delta G = \Delta G_x$ @ x and $\Delta G = \Delta G_\infty$ @ $x = \infty$.
(**b**) Plot the concentration C_x profile at two different temperatures. Let

$\phi_\infty = 0$	$\lambda = 0.2 \ cm^{-1}$
$\phi_o = 8.314x10^{-3} \ V$	$0 \le x \le 3.8 \ cm$
$T = 298^o K$ (___ curve)	$C_\infty = 1.57x10^{-3} \ mol/l = 0.1 \ g/l$
$T = 318^o K$ ($\cdots$ curve)	$F = 96,500 \ J/mol.V$

Solution:

a) *The oxidation reaction is $Cu = Cu^{+2} + 2e$. Combining eqs. (a) and (b) yields*

$$\int_{\mu_\infty}^{\mu_x} d\mu \quad = \quad -zF \int_{\phi x}^{\phi \infty} d\phi \tag{c}$$

$$\mu_x - \mu_\infty \quad = \quad -zF\phi_x \tag{d}$$

$$\mu_x - \mu_\infty \quad = \quad -zF\phi_o \exp\left(-\lambda x\right) \tag{e}$$

From eq. (2.27),

$$\Delta G_x \quad = \quad \mu_{x,prod} - \mu_{x,react} = \mu_{x,prod} \tag{f}$$

$$\Delta G_\infty \quad = \quad \mu_{\infty,prod} - \mu_{\infty,react} = \mu_{\infty,prod} \tag{g}$$

since $\mu_{x,prod} = \mu_{\infty,react} = 0$ for the oxidation reaction. From eq. (2.31b), the change

$$\Delta G_x \quad = \quad -RT \ln\left(K_x\right) = -RT \ln\left(C_x\right) \tag{h}$$

$$\Delta G_\infty \quad = \quad -RT \ln\left(K_\infty\right) = -RT \ln\left(C_\infty\right) \tag{i}$$

Combining eqs. (f) through (i) gives

$$\mu_x \quad = \quad -RT \ln\left(C_x\right) \tag{j}$$

$$\mu_\infty \quad = \quad -RT \ln\left(C_\infty\right) \tag{k}$$

$$\mu_x - \mu_\infty \quad = \quad RT \ln\left(\frac{C_\infty}{C_x}\right) \tag{l}$$

Finally, equating eqs. (e) and (l) yields

$$C_x \quad = \quad f(x,T) = C_\infty \exp\left[\frac{zF\phi_o}{RT} \exp\left(-\lambda x\right)\right] \tag{m}$$

$$C_x \quad = \quad (0.1 \ g/l) \exp\left[\frac{193}{T} \exp\left(-0.2x\right)\right] \tag{n}$$

$$C_x = (0.1 \ g/l) \exp[\tfrac{193}{T} \exp(-0.2x)]$$
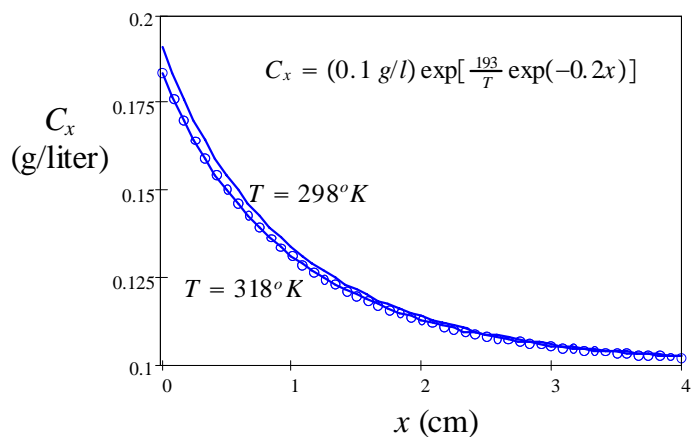
6.28 Derive an expression for $i_L = f(C_x, T, v_x)$ and explain its physical significance with respect to concentration polarization and metal reduction. Plot $\eta_c = f(i/i_L)$ when $i_L = 5 \times 10^{-3}$ A and $i_L = 10^{-2}$ A to support your explanation. When is the concentration polarization process discernible (apparent)?
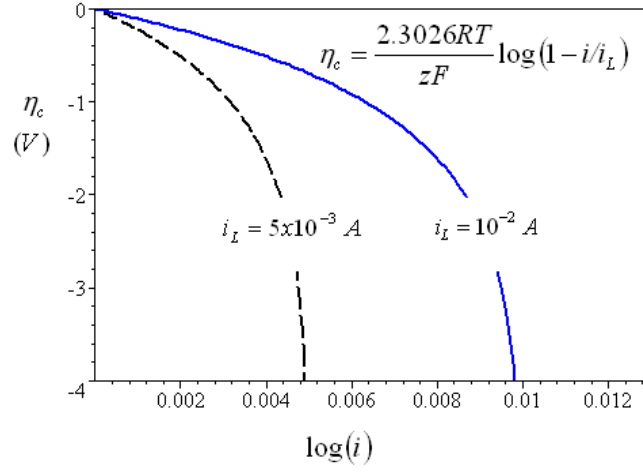
Solution:

Combining eqs. (6.92), (6.97), (6.72), *and* (6.76) *yields the sought expression along with the overpotential equation*

$$i_L = \frac{zF\kappa C_x v_x T}{F_x\sqrt{\pi D t}} = f(C_x, v_x, T) \qquad (a)$$

$$\eta_c = \frac{2.303RT}{zF} \log\left(1 - \frac{i}{i_L}\right) \qquad (b)$$

The schematic polarization diagram is shown below for two different cases.

$$\eta_c = \frac{2.3026RT}{zF}\log\left(1 - i/i_L\right)$$

$$i_L = 5\text{x}10^{-3}\ A \qquad i_L = 10^{-2}\ A$$

Thus, $i_L = f(C_x, v_x, T)$ represents the maximum rate of reduction, and it is the limiting diffusion current density. In fact, $i_L = f(C_x, v_x, T)$ is significant during reduction processes and negligible during metal dissolution. With respect to $i_L = f(C_x, v_x, T)$, it increases with increasing concentration, species velocity and temperature as predicted by equation (a). Finally, concentration polarization becomes apparent when $i \to i_L$ and $\eta_c \to \infty$ and $\eta_c \to 0$ when $i_L \to \infty$. The latter can be defined as

$$\eta_c = \frac{2.303RT}{zF}\log\left(1 - \frac{iF_x\sqrt{\pi Dt}}{zF\kappa C_x v_x T}\right) \qquad (c)$$

It is also apparent that concentration polarization is possible when $|\eta_c| > 0$ due to presence of F_x for ionic mobility at an ionic velocity v_x.

Chapter 7

CORROSIVITY AND PASSIVITY

7.1 PROBLEMS

7.1 Determine **(a)** the electric potential E in millivolts, **(b)** the time in seconds, and **(c)** the growth rate in $\mu m/s$ for electroplating a 3-μm thick Cr film on a Ni-undercoated steel part, provided that the electrolyte contains 10^{-4} mol/l of Cr^{+3} cations at 25^oC, the Ni-steel part has a 10-cm^2 surface area, and the cell operates at 50% current efficiency and at a passive current of 0.8 amperes. Assume that the oxide passive film has a density of 7.19 g/cm^3.

Solution:

$Cr^{+3} + 3e = Cr$ $E^o_{Cr} = -0.744$ V $z = 3$ $x = 3x10^{-4}$ cm

$\rho = 7.19$ g/cm^3 $A_{w,Cr} = 52$ g/mol $i = I/A_s = 0.08$ A/cm^2

$A_s = 10$ cm^2 $\epsilon = 0.50$ $[Cr^{+3}] = a_{Cr^{+3}} = 10^{-4}$ mol/l

(a) *Using Nernst equation yields*

$$E \;>\; E_o = E^o + \frac{RT}{zF} \ln\left(a_{Cr^{+3}}\right)$$

$$E \;>\; E_o = -0.744V + \frac{(8.314\ J/mol.K)\,(298\ K)}{(3)\,(96,500\ J/mol.V)} \ln\left(10^{-4}\right)$$

$$E \;>\; E_o = -0.823\ V$$

(b) *Integrating equation eq. (7.21) yields the time*

$$t \;=\; \int_0^x \left(\frac{zF\rho}{\epsilon i A_w}\right) dx = \frac{zF\rho x}{\epsilon i A_w}$$

$$t \;=\; \frac{(3)\,(96,500\ A.s/mol)\,\left(7.19\ g/cm^3\ \right)\,\left(3x10^{-4}\ cm\right)}{(0.50)\,(0.08\ A/cm^2)\,(52\ g/mol)}$$

$$t \;=\; 300.22\ \text{sec} \simeq 5\ \text{min}$$

(c) *The film growth rate is*

$$\frac{dx}{dt} = \frac{\Delta x}{\Delta t} = \frac{3\ \mu m}{300.22\ \sec}$$

$$\frac{dx}{dt} = 0.01\ \frac{\mu m}{\sec}$$

7.2 **(a)** If chromiun oxide film frow rate is 0.03 $\mu m/\sec$, how long will it take to grow a 5 μm film on a Ni-substrate. Assume that the cell operates at 50% current efficiency. Calculate **(b)** the current density.

Solution:
(a) *The time is*

$$\frac{dx}{dt} = \frac{\Delta x}{t}$$

$$t = \frac{\Delta x}{dx/dt} = \frac{5\mu m}{0.05\ \mu m/\sec} = 100\ \sec$$

(b) *From eq.(7.51), the current density is*

$$i = \frac{zF\rho x}{\epsilon t A_w} = \frac{(3)\,(96500)\,(7.19)\left(5\times 10^{-4}\right)}{(0.8)\,(100)\,(52)}$$

$$i = 0.25\ A/cm^2$$

7.3 Briefly, explain why the corrosion rate and the corrosion potential increase on the surface of some metallic materials in contact with an oxygen-containing acid solution. In this situation oxygen acts as an oxidizer. Use a schematic polarization diagram to support your explanation. Let the exchange current densities and the open-circuit potentials be $i_{o,O_2} < i_{o,H_2} < i_{o,M}$ and $E_{o,O_2} > i_{o,H_2} > i_{o,M}$. What effect would have oxygen on the metal dissolution if $i_{o,O_2} << i_{o,H_2} < i_{o,M}$ and $E_{o,O_2} > i_{o,H_2} > i_{o,M}$.
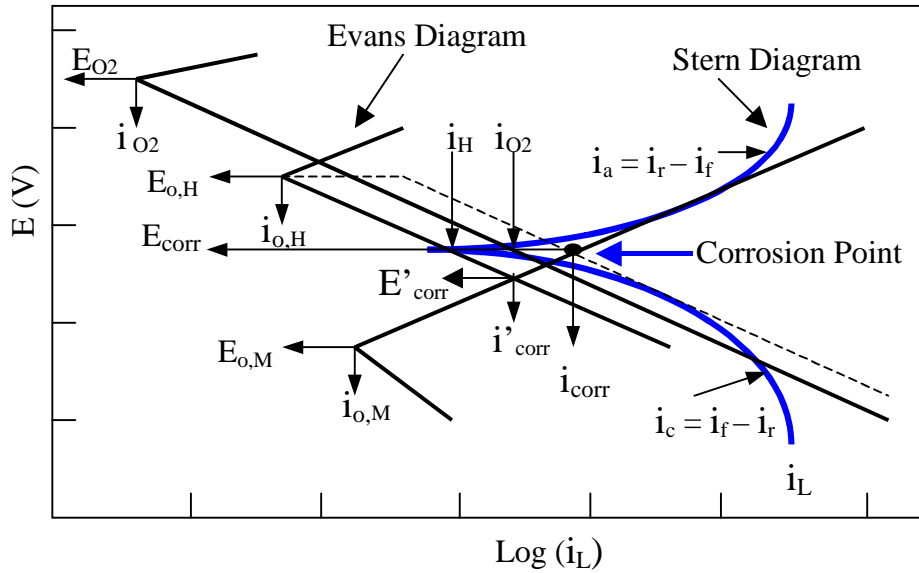
Solution:

NO OXYGEN: *The polarization diagram below implicitly explain the reason why the corrosion rate increases in the presence of oxygen in an acid solution. According to the figure below, the corrosion rate in terms of current density and the corrosion potential are*

$$i'_{corr} = i'_H \qquad\qquad \text{No oxygen}$$

$$i'_{net} = i'_{corr} - i'_H = 0 \quad \text{at equilibrium}$$

$$E'_{corr} = E'_H \qquad\qquad \text{No oxygen}$$

WITH OXYGEN: *However, when oxygen is present as an oxidizer the corrosion rate and corrosion potential become*

$$
\begin{aligned}
i_{corr} &= (i_H + i_{O_2}) > i'_{corr} \\
E_{corr} &> E'_{corr}
\end{aligned}
$$

Consequently, hydrogen evolution decreases because $i_H < i'_H$ and oxygen evolution evolves consuming additional electrons from the metal. In certain cases when $i_{o,O_2} \ll i_{o,H_2} < i_{o,M}$ the presence of oxygen as an oxidizer would have insignificant effect on the rate of metal dissolution.

7.4 Assume that a stainless steel pipe is used to transport an aerated acid solution containing $1.2x10^{-6}$ mol/cm^3 of dissolved oxygen at room temperature and that the electric-double layer is 0.7 mm and 0.8 mm under static and flowing velocity, respectively. If the critical current density for passivation and the diffusion coefficient of dissolved oxygen are 300 $\mu A/cm^2$ and 10^{-5} cm^2/s, then determine **(a)** whether or not corrosion will occur under the given conditions and **(b)** the passive film thickness at 5-*minute* exposure time if $i_p = 50$ $\mu a/cm^2$. Also assume that the density of the film and the molecular weight of the stainless steel are 7.8 g/cm^3 and 55.85 g/mol, respectively and that the predominant oxidation state is 3. Given data:

Solution:
Given data:

$$F = 96,500 \; A.s/mol \qquad\qquad C_x = 1.2x10^{-6} \; mol/cm^3$$
$$z = 3 \qquad\qquad\qquad\qquad \delta(static) = 0.07 \; cm$$
$$D = 10^{-5} \; cm^2/s \qquad\qquad \delta(flowing) = 0.008 \; cm$$
$$i_{crit} = 300 \; \mu A/cm^2 \qquad\qquad \rho = 7.8 \; g/cm^3$$

The reduction reaction is

$$O_2 + 2H_2O + 4e = 4OH^- \quad with \quad E_{O_2}^o = 0.401 \; V_{HSE}$$

(a) *From eq. (6.99), the limiting current density for both conditions is*

$$i_L = \frac{zFDC_x}{\delta} = \frac{3\,(96500\;A.s/mol)\left(10^{-5}\;cm^2/s\right)\left(1.2x10^{-6}\;mol/cm^3\right)}{0.07\;cm}$$
$$i_L \simeq 49.63 \; \mu A/cm^2 < i_{crit} \; \textit{for corrosion under static solution}$$
$$i_L \simeq 43.43 \; \mu A/cm^2 > i_{crit} \; \textit{for passivation under flowing solution}$$

(b) *The limiting current density for passivation under flowing solution be-comes the passive current density, then the passive film thickness can be esti-mated using eq. (7.51) along with a density of 7.8 g/cm^3 and a molecular weight of 55.85 g/mol. Hence,*

$$x = \frac{i_p A_w t}{zF\rho}$$
$$x = \frac{\left(50x10^{-6}\;A/cm^2\right)(55.85\;g/mol)\,(300\;s)}{(3)\,(96,500\;A.s/mol)\,(7.8\;g/cm^3)}$$
$$x = 0.371 \; \mu m = 371 \; nm$$

This is a reasonable result despite the crude approximation technique being used in this example problem. The passive oxide film may be $CrO_x(OH)_{3-2x}.nH_2O$ as per Figure 7.20.

7.5 For the reinforced concrete specimen (concrete slab) shown in Example 7.2, calculate (a) the chloride ion penetration depth (x) when the potential gradient due to diffusion and migration are equal and (b) the potential gradients. [Solution: (a) $x = 1.03 \; mm$].

Solution:
(a) *From eqs. (6.12) and (6.13),*

$$\left(\frac{d\phi}{dx}\right)_{diffusion} = \frac{RT}{xF}$$
$$\left(\frac{d\phi}{dx}\right)_{electric} = \frac{E}{L}$$

Equating these equation yields

$$x = \frac{RTL}{EF} = \frac{(8.314)(298)(8)}{(2)(96500)} = 1.03 \ mm$$

Then the potential gradients are

$$\left(\frac{d\phi}{dx}\right)_{electric} = \left(\frac{d\phi}{dx}\right)_{diffusion} = \frac{RT}{xF} = \frac{(8.314)(298)}{(0103)(96500)}$$

$$\left(\frac{d\phi}{dx}\right)_{electric} = \left(\frac{d\phi}{dx}\right)_{diffusion} = 2.49 \times 10^{-4} \ V/cm$$

7.6   For a reinforced concrete slab having a concrete cover 50-*mm* deep, the threshold and the surface concentrations of chloride anions are $C_{th} = 0.60$ Kg/m^3 and $C_s = 19 \ Kg/m^3$. Also, $D = 32 \ mm^2/yr$ is the diffusivity of chloride anions. Determine (a) the chloride molar flux, (b) the time (T_i) to initiate corrosion on an uncoated reinforcing steel surface (Figure 7.21c). Explain. (c) Plot the concentration profile of chloride anions at the corrosion initiation time T_i. Calculate (d) the rate of iron hydroxide $Fe(OH)_2$ production (molar flux and mass flux) at the anodic regions for an anodic current density of 1.5 $\mu A/cm^2$, (e) the corrosion rate (C_R) of steel in mm/yr, (f) the time required for cracking and spalling due to the formation of a critical rust $(Fe(OH)_3)$ volume if the bar diameter is reduced only 25 μm and (g) the time for repair and the apparent mass of rust per area.

Solution:

**(a)** *The chloride molar flux at* $t_i = 11$ *years can be calculated using eq. (6.8). Thus,*

$$J_{Cl^-} = \frac{i}{zF} = \frac{1.5 \ \mu A/cm^2}{(1)(96,500 \ A.s/mol)} \simeq 1.5510^{-11} \ \frac{mol}{cm^2.\sec}$$

(b) *The time to initiate corrosion, eq. (7.63), is*

$$t_i = \frac{x^2}{4D}\left[\text{erf}^{-1}\left(1 - \frac{C_{th}}{C_s}\right)\right]^{-2}$$

$$t_i = \frac{(50 \ mm)^2}{4(31.61 \ mm^2/yr)}\left[\text{erf}^{-1}\left(1 - \frac{0.6 \ Kg/m^3}{18 \ Kg/m^3}\right)\right]^{-2}$$

$$t_i \simeq 13.43 \ years$$

(c) *The concentration profile of chloride ions,* $C(x, t_i)$ *at the approximated initiation time of* 13.43 *years can be determined using the solution of Fick's second law of diffusion, eq. (7.59).*

$$
\begin{aligned}
C\left(x,t\right) &= C_s \left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right] & (7.59) \\
C\left(x,t\right) &= \left(19\ Kg/m^3\right)\left[1 - \operatorname{erf}\left(\frac{10x}{2\sqrt{\left(32\ mm^2/yr\right)\left(13.43\ yr\right)}}\right)\right] \\
C\left(x,t\right) &= y = 19.0\,\operatorname{erfc}\left(0.241\,19x\right)
\end{aligned}
$$
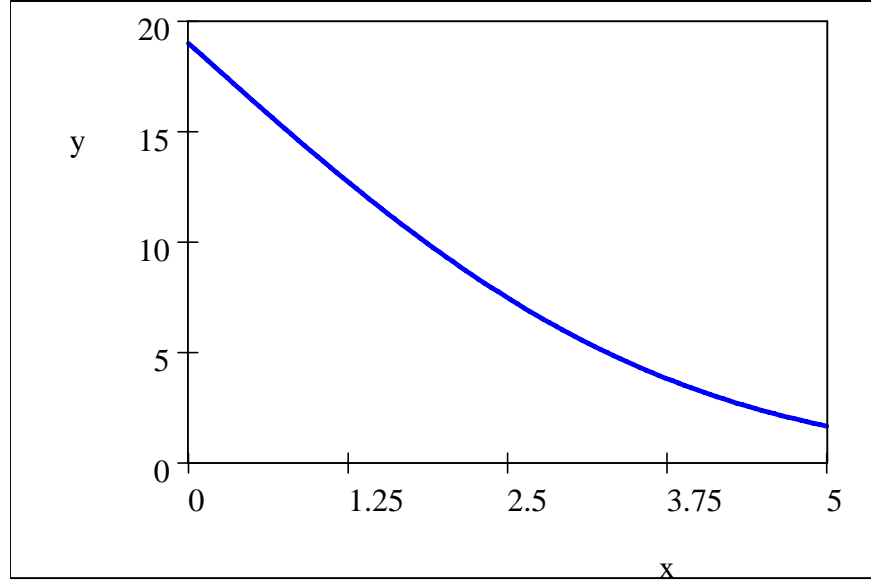
(d) *From eq. (7.69) along with* $i_a = i_{corr}$,

$$
\begin{aligned}
J_{Fe(OH)_2} &= \frac{i_{corr}}{zF} = \frac{1x10^{-6}\ A/cm^2}{(2)(96500\ A.\sec/mol)} \\
J_{Fe(OH)_2} &= 5.18 \times 10^{-12}\ mol/\left(cm^2.\sec\right)
\end{aligned}
$$

Multiplying this result by the iron molar mass, 55.85 g/mol, yields

$$
\begin{aligned}
J_{Fe(OH)_2} &= 2.893 \times 10^{-10}\ g/\left(cm^2.\sec\right) = 9.123 \times 10^{-3}\ g/\left(cm^2.yr\right) \\
J_{Fe(OH)_2} &\simeq 91.23\ g/\left(m^2.yr\right) \simeq 0.091\ Kg/\left(m^2.yr\right)
\end{aligned}
$$

Thus, the rate of rust $[Fe(OH)_3]$ *production, eq. (7.68), is*

$$J_{Fe(OH)_3} = \left[\frac{M_{Fe(OH)_3}}{M_{Fe(OH)_2}}\right] J_{Fe(OH)_2} \quad \text{(Rust)}$$

$$J_{Fe(OH)_3} = \left(\frac{106.85 \ g/ml}{89.85 \ g/mol}\right) \left[91.23 \ g/\left(m^2.yr\right)\right]$$

$$J_{Fe(OH)_3} \simeq 108.49 \ g/\left(m^2.yr\right) \quad \text{(Rust)}$$

(e) *The uniform corrosion rate* (C_R) *of ferrous ions* (Fe^{2+}), *eq. (7.74) at the end of the 11th year*

$$C_R = \frac{i_a A_w}{zF\rho} = \frac{\left(1.5 \times 10^{-6} \ A/cm^2\right)\left(55.85 \ g/mol\right)}{(2)\left(96500 \ A.sec/mol\right)\left(7.86 \ g/cm^3\right)}$$

$$C_R = 5.5225 \times 10^{-11} \ cm/\sec \simeq 0.017 \ mm/yr$$

$$C_R = 17 \ \mu m/yr$$

Therefore, the corrosion rate, 127 $\mu m/yr$, *is rather low, but sufficient to be noticed after* 13.43 *years. This corrosion rate corresponds to pitting formation at the 13th year; however, if the chloride ion supply continues, then the corrosion eventually propagates.*

(f) *If the reduction in diameter of the uncoated steel bar is* 25 μm, *then the time for some rust formation that causes cracking and spalling, eq. (7.64), is*

$$t_c = \frac{25 \ \mu m}{17 \ \mu m/yr} = 1.47 \ yr$$

(g) *The repair time, eq. (7.65), is*

$$t_r = t_i + t_c = 13.43 \ yr + 1.47 \ yr$$

$$t_r = 14.9 \ yr$$

Therefore, the first concrete repair is required at 14.9 *years. On the other hand, The apparent mass of rust per area is*

$$m_{rust} = J_{rust}.t_c = \left[108.49 \ g/\left(m^2.yr\right)\right](1.47 \ yr)$$

$$m_{rust} = 159.48 \ g/m^2 = 0.159 \ g/cm^2$$

7.7 Assume that all electrochemical reactions are governed by the Nernst equation, which specifies the relationship between the potential of an electrode and the concentrations of the two species Fe^{3+} and Fe^{+2} involved in the reversible redox reaction at the working electrode. Assume a hydrogen-rich electrolyte. (a) Write down the electrochemical reaction for Fe^{3+} and Fe^{2+} and

the potential equation. **(b)** What is the driving force when the concentrations of the species at the working electrode surface are equal? **(c)** What is the driving force at the working electrode surface when $C_{Fe^{3+}}(\infty, t) > 2C_{Fe^{3+}}(0, t)$ and $C_{Fe^{2+}}(0, t) = 0.5C_{Fe^{3+}}(0, t)$, where $t > 0$ at $25^o C$? **(d)** Derive the current equation for the case described in part (c). Recall that the current is simply the flow rate of electrons. **(e)** Draw schematic concentration profiles for $C_O = C_{Fe^{3+}}$ when $I = 0$, $I > 0$ for reduction (Fe^{3+} cation moves to the electrode surface) and $I < 0$ for oxidation so that the Fe^{3+} cation moves away from the electrode surface.

Solution:

(a) The electrochemical reaction for O and R and the potential equation are

$$
\begin{aligned}
O + ze^- &= R \\
Fe^{3+} + e^- &= Fe^{2+} \quad \text{for } z = 1 \\
E &= E^o - \frac{RT}{zF} \ln\left(\frac{C_{Fe^{2+}}}{C_{Fe^{3+}}}\right)
\end{aligned}
$$

(b) There is no driving force because $C_{Fe^{3+}} = C_{Fe^{2+}}$ and $E = E^o$ since $\ln\left(C_{Fe^{2+}}/C_{Fe^{3+}}\right) = \ln(1) = 0$. Therefore, there is no driving force for transport of analyte to or from the working electrode surface.

(c) For $C_{Fe^{3+}}(\infty, t) > 2C_{Fe^{3+}}(0, t)$,

$$
\begin{aligned}
Fe^{3+} + e^- &= Fe^{2+} \quad \text{for } z = 1 \\
E &= E^o - \frac{RT}{zF} \ln\left(\frac{C_{Fe^{2+}}(0, t)}{C_{Fe^{3+}}}\right) \\
E &= E^o - \frac{RT}{zF} \ln\left(\frac{0.5C_{Fe^{3+}}(0, t)}{C_{Fe^{3+}}}\right) \\
E &= E^o - \frac{RT}{zF} \ln(0.5)
\end{aligned}
$$

From Table 2.2, $E^o = 0.77 \ V_{SHE}$ and the driving force is

$$
\begin{aligned}
E &= 0.44 \ V_{SHE} - \frac{\left(8.314510 \ J.mol^{-1}K^{-1}\right)(298 \ K)}{(1)\left[96,500 \ J/\left(mol.V_{SHE}\right)\right]} \ln(0.5) \\
E &= 0.46 \ V_{SHE}
\end{aligned}
$$

(d) The current equation at the working electrode surface ($x = 0$) is

$$
\begin{aligned}
J &= -D\left(\frac{\partial C}{\partial x}\right)_{x=0} \\
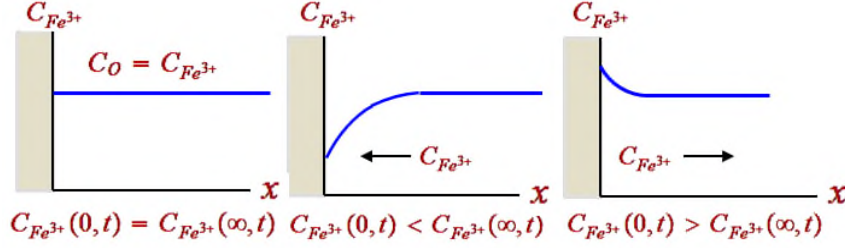Q &= zFN
\end{aligned}
$$

Figure 7.1:

where N is the mole number. Then, the fundamental relationship for the current in any amperometric experiment derived as

$$I = \frac{dQ}{dt} = -zFA_sJ = zFA_sD\left(\frac{\partial C}{\partial x}\right)_{x=0}$$

(e) The schematic concentration profiles for $C_O = C_{Fe^{3+}}$ is

7.8 Consider the reversible reaction $O + ze^- = R$ (as in $Fe^{3+} + e^- = Fe^{2+}$) for deriving the half-wave potential ($E_{1/2}$) using $I = 0.5I_L$, where I_L is the limiting current for a voltammogram. Assume that the initial solution contains only the species O and that diffusion is the form of mass transport so that the current in a voltammetric cell is

$$\begin{align}
I &= K_O\left([O]_b - [O]_{x=0}\right) \tag{a} \\
I &= K_R\left([R]_{x=0} - [R]_b\right) = K_R[R]_{x=0} \tag{b}
\end{align}$$

where $K_O = zFA_sD_O/\delta$ and $K_R = zFA_sD_R/\delta$, $[R]_b = 0$ in the bulk solution initially. Use the Nernst equation for defining the voltammetric cell potential. Recall that the applied potential reduces O to R and that the current depends on the rate at which O diffuses through the diffusion layer (δ).

Solution:

The Nernst equation gives the potential at the electrode surface. Thus,

$$E = E^o - \frac{RT}{zF}\ln\frac{[R]_{x=0}}{[O]_{x=0}} \tag{c}$$

Initially, $[O]_{x=0} = 0$ in eq. (a) so that the current becomes the limiting current (I_L)

$$I_L = K_O[O]_b \tag{d}$$

From eqs. (b) and (d),

$$[R]_{x=0} = \frac{I}{K_R} \tag{e}$$

Substitute eq. (d) into (a) yields

$$I \quad = \quad I_L - K_O\,[O]_{x=0}$$
$$[O]_{x=0} \quad = \quad \frac{I_L - I}{K_O} \tag{f}$$

Substitute eqs. (e) and (f) into (c) gives

$$E \quad = \quad E^o - \frac{RT}{zF}\ln\frac{[R]_{x=0}}{[O]_{x=0}}$$
$$E \quad = \quad E^o - \frac{RT}{zF}\ln\left(\frac{I}{K_R}\frac{K_O}{I_L - I}\right)$$
$$E \quad = \quad E^o - \frac{RT}{zF}\ln\left[\left(\frac{K_O}{K_R}\right)\left(\frac{I}{I_L - I}\right)\right]$$

and

$$E = E^o - \frac{RT}{zF}\ln\left(\frac{K_O}{K_R}\right) - \frac{RT}{zF}\ln\left(\frac{I}{I_L - I}\right)$$

Use $I = 0.5 I_L$ to get $E = E_{1/2}$ and

$$E_{1/2} = E^o - \frac{RT}{zF}\ln\left(\frac{K_O}{K_R}\right)$$

since $\ln\left[I/\left(I_L - I\right)\right] = \ln\left[0.5 I_L/\left(I_L - 0.5 I_L\right)\right]\ln\left[1\right] = 0$. Hence,
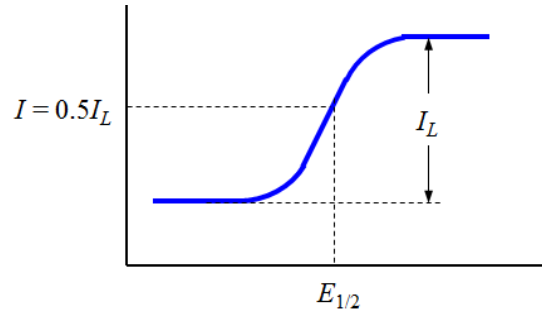
Chapter 8

DESIGN AGAINST CORROSION

8.1 PROBLEMS/QUESTIONS

CATHODIC PROTECTION

8.1 Why cathodic protection is not generally recommended for stress corrosion problems on high-strength ferritic steels?

Answer: *Hydrogen embrittlement may be the main cause of corrosion on ferritic steel cathodes when the hydrogen evolution occurs. In this case, cathodically discharged atomic hydrogen readily diffuses into the iron matrix, specifically in voids, making the steel susceptible to hydrogen embrittlement due to a high pressure (P) build-up by molecular hydrogen within voids. This phenomenon may be represented by the reaction $H + H \rightarrow H_2$. If $P > \sigma_{ys}$ (yield strength), then the steel loses its strength and ductility.*

8.2 A steel structure exposed to seawater is to be cathodically protected using the sacrificial anode technique. calculate a) the number of Zn anodes (N) that will be consumed in a *year* if the Zn anode capacity is 770 $A.h/Kg$ (average value as per Table 8.2) and the current is 0.70 *amps*, and b) the individual weight (M) of anodes so that $NM \geq W$, where W is the total theoretical weight of the anodes.

Solution:

$$Zn = Zn^{+2} + 2e$$
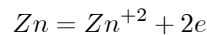
$C_a = 770 \ A.h/Kg = 2.772x10^6 \ A.s/Kg$	
$t = 1 \ year = 31.536x10^6$ sec	
$A_w = 65.37 \ g/mol$	$I = 0.7 \ A$
$z = 2$	$F = 96,500 \ A.s/mol$

Using Faraday's law, Eq. (3.12c) *or* (8.60), *the total theoretical weight of anodes is*

$$W = \frac{It A_w}{zF}$$

$$W = \frac{(0.70 \ A)\left(31.536x10^6 \ s\right)(65.37 \ g/mol)}{(2)(96,500 \ A.s/mol)}$$

$$W = 7.48 \ Kg$$

Using the anode life $(L_d = t)$ *equation given in Table 8.4 yields the theoretical number of anodes. Hence,*

$$N = \frac{7C_a A_w}{3\pi z F}$$

$$N = \frac{(7)\left(2.772x10^6 \ A.s/Kg\right)(65.37 \ g/mol)}{(3\pi)(2)(96,500 \ A.s/mol)}$$

$$N \simeq 1$$

Then,

$$M > \frac{W}{N} = 7.48 \ Kg$$

8.3 Cathodically protect a vertical pressurized steel tank ($\sigma_{ys} = 414 \ MPa$ and $P = 12 \ MPa$) using one flush mounted Mg-Al-Zn bracelet ($B_i = 0.9525$ cm). Assume 2% tank coating damage per year and neglect any installation damage if the tank is coated after installation. Use a bracelet with dimensions equal to $(0.50 \ cm) \ x \ (3 \ cm) \ x \ (6 \ cm)$. Calculate **(a)** the maintenance current and current density if the initial current density and the design lifetime are $0.43 \ \mu A/cm^2$ and 25 $years$. Will it be convenient to protect the tank having a thickness of 1.8 cm? The tank height and the internal diameter are 65 cm and 15.24 cm, respectively. **(b)** Will the tank explode at the end of the anode life time? Assume that the anode Mg-alloy and $\rho_x = 5,000 \ ohm.cm$ for the soil. Given data for the Mg-alloy anode: $\rho = 1.74 \ g/cm^3$, $A_w = 24.31 \ g/mol$ and $C_a = 1,230 \ A.h/Kg$ for the Mg-Al-Zn anode (Table 8.2).

Solution:
The tank and the anode surface areas are, respectively

$$A_t = \pi d_i h_t = (\pi)(15.24 \ cm)(25.40 \ cm)$$

$$A_t = 1,216 \ cm^2$$

$$A_a = NwL = (1)(3 \ cm)(6 \ cm) = 18 \ cm^2$$

The initial current for polarizing the structure is

$$I_i = A_a i = \left(18 \ cm^2\right)\left(0.43 \ \mu A/cm^2\right) = 7.74 \ \mu A$$

From Table 8.4, the average initial weight of the anode is

$$W_i = \frac{3\pi I_i L_d}{7C_a}$$

$$W_i = \frac{(3\pi)\left(7.74x10^{-6}\ A\right)(219,000\ h)}{(7)\left(1,230\ A.h/Kg\right)}$$

$$W_i = 1.86\ grams$$

From Table, 8.5, the anode electrical resistance is

$$R_f = \frac{\pi\rho_x}{10\sqrt{A_a}}$$

$$R_f = \frac{(\pi)\left(5x10^3 ohm,cm\right)}{10\sqrt{18\ cm^2}} = 370.24\ ohm$$

Using Ohm's law yields the initial potential (E_i) *using a rectifier having a capacity greater than* E_i

$$E_i = I_i R_f = \left(7.74x10^{-6}\ A\right)(370.24\ ohm)$$

$$E_i = 2.87\ mV$$

$$E_{rect} > E_i$$

From Table 8.3, the polarized current density is chosen as $0.5\ \mu A/cm^2$ *so that*

$$I_p = A_a i_p = \left(18\ cm^2\right)\left(0.5\ \mu A/cm^2\right) = 9\ \mu A$$

The final current for maintaining the structure polarized and cathodically protected is

$$I_f = (1 - \lambda_i - \lambda_c L_d)(A_a i) \qquad (8.61)$$

$$I_f = 1\left[1 - 0 - \left(\frac{2\%}{100\%}\right)(25)\right](A_a i)$$

$$I_f = 0.5 A_a i = 0.5 I_i$$

$$I_f = (0.5)\left(18\ cm^2\right)\left(0.43\ \mu A/cm^2\right) = 3.87\ \mu A$$

For maintenance, the current and the final current density are, respectively

$$\bar{I} = \frac{I_p + I_f}{2} = \frac{9\ \mu A + 3.87\ \mu A}{2} = 6.44\ \mu A$$

$$i_f = \frac{\bar{I}}{A_a} = \frac{6.44\ \mu A}{18\ cm^2} = 0.36\ \mu A/cm^2$$

Finally, the maintenance or final potential is

$$E_f = \bar{I} R_f = \left(6.44x10^{-6}\ A\right)(370.24\ V/A)$$

$$E_f = 2.38\ mV$$

a) *There will be a potential drop and a current change of*

$$\Delta E = E_i - E_f = E_i = 2.87mV - 2.38 \ mV = 0.49 \ mV$$
$$\Delta I = I_i - \overline{I} = 7.74 \ \mu A - 6.44 \ \mu A = 1.30 \ \mu A$$

Both ΔE and ΔI represent a 17% reduction. Therefore, it is convenient to cathodically protect the steel tank. The initial and final corrosion rates of the anode in terms of current density are 0.43 $\mu A/cm^2$ and 0.36 $\mu A/cm^2$, respectively. The initial corrosion rate of the anode in mm/y is

$$C_{R,i} = \frac{i_i A_w}{zF\rho} = \frac{(0.43x10^{-6} \ \mu A/cm^2)(24.31 \ g/mol)}{(2)(96,500 \ A.s/mol)(1.74 \ g/cm^3)}$$
$$C_{R,i} = 3.11x10^{-11} \ cm/s = 0.0010 \ mm/y$$

and the final corrosion rate becomes

$$C_{R,,f} = \frac{i_f A_w}{zF\rho} = \frac{(0.36x10^{-6} \ \mu A/cm^2)(24.31 \ g/mol)}{(2)(96,500 \ A.s/mol)(1.74 \ g/cm^3)}$$
$$C_{R,,f} = 2.61x10^{-11} \ cm/s = 0.0008 \ mm/y$$

b) *The final thickness of the Mg-alloy anode is $B_f = (0.0008 \ mm/y)(25 \ y) = 0.02 \ mm$, which is a thin foil and it must be replaced by a new anode.*
The hoop stress in the steel tank is

$$\sigma_h = \frac{Pd}{2B} = \frac{(12 \ MPa)(15.24 \ cm)}{2(1.8 \ cm)} = 50.8 \ MPa$$
$$\sigma_h \ << \ \sigma_{ys}$$

As a result, he steel tank will not deform neither explode because $\sigma_h << \sigma_{ys}$ and there are no cracks; therefore, it will not corrode at all the end of the design life of 25 years.

8.4 A 2-m diameter steel tank containing water is pressurized at 200 kPa. The hoop stress, thickness, and height are $420MPa$, 2 cm, and 8 cm, respectively. If the measured corrosion rate is 0.051 mm/y, determine a) the tank life and b) the developed current. Data: $\rho = 7.86 \ g/cm^3$ and $A_w = 55.86 \ g/mol$.

Solutions:

$$Fe \rightarrow Fe^{+2} + 2e$$
$$P = 200 \ kPa \qquad d = 2 \ m$$
$$\sigma = 420 \ MPa \qquad B = 2 \ cm$$
$$C_R = 0.051 \ mm/y \quad h = 8 \ m$$

a) *From eq. (8.64),*

$$C_R = \frac{iA_w}{zF\rho} = \frac{Pd}{2\sigma t} \tag{8.64}$$

$$t = \frac{Pd}{2\sigma C_R} = \frac{(200 \ kPa) \left(2x10^3 \ mm\right)}{(2) \left(420,000 \ kPa\right) \left(0.051 \ mm/y\right)}$$

$$t = 9.34 \ years = 2.94x10^8 \ sec$$

b) *From eq. (8.61),*

$$i = \frac{zF\rho B}{tA_w} \tag{8.63}$$

$$i = \frac{(2) \left(96,500 \ A.s/mol\right) \left(7.86 \ g/cm^3\right) (2 \ cm)}{\left(2.94x10^8 \ s\right) \left(55.85 \ g/mol\right)}$$

$$i = 1.84x10^{-4} \ A/cm^2 = 184 \ \mu A/cm^2$$

For a lateral area $A_s = \pi dh$, the current becomes

$$I = A_s i = \pi dhi$$
$$I = (\pi) \left(2x10^2 \ cm\right) \left(8x10^2 \ cm\right) \left(1.84x10^{-4} \ A/cm^2\right)$$
$$I = 92.49 \ A$$

8.5 **(a)** Derive eq. (8.58) and **(b)** calculate the theoretical anode capacity (C_a) for magnesium (Mg) and zinc (Zn).

Solutions:

(a) *From eqs. (5.30) with $\epsilon = 1$ and Table 8.4,*

$$m = \frac{ItA_w}{zF} \quad \text{eq. (5.30)}$$

$$W = \frac{3\pi It}{7C_a} \quad \text{Table 8.4}$$

Let $m = W$ since both represent mass. Thus, the anode capacity equations is

$$\frac{ItA_w}{zF} = \frac{3\pi It}{7C_a}$$

$$C_a = \frac{3\pi zF}{7A_w}$$

(b) *Anode capacity for Mg and Zn:*

$$Mg = Mg^{+2} + 2e$$

$$C_{a,Mg} = \frac{3\pi zF}{7A_w} = \frac{(3\pi)\,(2)\,(96,500\ A.s/mol)}{(7)\,(24.31\ g/mol)}$$

$$C_{a,Mg} = 2,969\ \frac{A.h}{Kg}$$

and

$$Zn = Zn^{+2} + 2e$$

$$C_{a,Zn} = \frac{3\pi zF}{7A_w} = \frac{(3\pi)\,(2)\,(96,500\ A.s/mol)}{(7)\,(65.37\ g/mol)}$$

$$C_{a,Zn} = 1,104\ \frac{A.h}{Kg}$$

8.6 Show that $\alpha = \sqrt{R_s/R_L}$.

Solution:

From eq. (8.20),

$$\eta_x = \eta_o \exp\left(-\alpha x\right) \tag{8.20}$$

$$\frac{d\eta_x}{dx} = -\alpha \eta_o \exp\left(-\alpha x\right) \tag{a}$$

$$\frac{d^2\eta_x}{dx^2} = \alpha^2 \eta_o \exp\left(-\alpha x\right) \tag{b}$$

*Substituting eqs.* (a) *and* (b) *into* (8.18) *yields*

$$\frac{d^2\eta_x}{dx^2} = \left(\frac{R_s}{R_L}\right)\eta_x \tag{8.18}$$

$$\alpha^2 \eta_o \exp\left(-\alpha x\right) = \left(\frac{R_s}{R_L}\right)\eta_o \exp\left(-\alpha x\right) \tag{c}$$

$$\alpha = \sqrt{\frac{R_s}{R_L}} \tag{d}$$

8.7 Use an annealed (@ 792^oC) 1040 steel plate of $B = 0.635\ cm$ thickness to design a cylindrical pressurized vessel using a safety factor (S_F) of 2. The annealed steel has a yield strength of 355 MPa. Calculate **(a)** the average allowable pressure according to the theory for thin-walled vessels. Will the vessel fail when tested at 2 MPa for 10 minutes? If it does not fail, then proceed to cathodically protect the cylindrical pressure vessel as a domestic or home water heater having a cylindrical magnesium (Mg) anode rod. All

dimensions shown below. Calculate **(b)** the applied hoop stress, the current, the potential for polarizing the heater and the resistance of the system, **(c)** the theoretical anode capacity and the anode lifetime of the anode in years and **(d)** how much electric energy will delivery the Mg anode rod? The steel vessel has a 98% internal glass coating (vitreous porcelain enamel lining) for protecting the steel inner wall against the corrosive action of portable water. Assume a water column of 76.20 cm and an internal pressure of 1 MPa. Assume that the exterior surface of the steel vessel is coated with an appropriate paint for protecting it against atmospheric corrosion and that the anode delivers 1.5 $V_{Cu/CuSO_4}$. The $NACE$ recommended potential for steels is -85 $V_{Cu/CuSO_4}$.
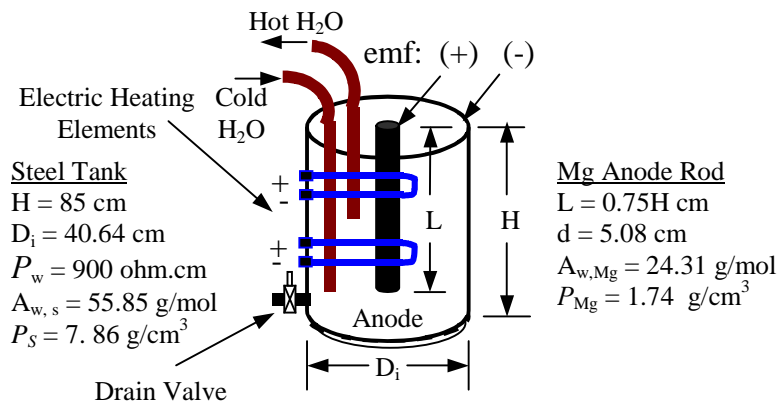
Solution:

(a) *The design hoop stress (tangential stress) is given*

$$\sigma = \frac{\sigma_{ys}}{S_F} = \frac{355\ MPa}{2} = 177.50\ MPa$$

The hoop stress (average tangential stress) equation is used for determining the average allowable pressure

$$\sigma = \frac{PD_i}{2B}$$

$$P = \frac{2B\sigma}{D_i} = \frac{(2)\,(0.635cm)\,(177.50\ MPa)}{40.64\ cm} = 5.55\ MPa$$

Assuming that the pressure vessel, as well as the glass coating, is crack-free one can deduce that the pressure vessel will not fail because $P > P_{test} = 2\ MPa$.

(b) *Since the steel major element is iron, the reaction $Fe^{+2} + 2e = Fe$ is assumed in this problem. Using eqs. (8.66) and (8.65) yield the applied hoop stress and the protective current density, respectively*

$$\sigma = \frac{PD_i}{2B} = \frac{(1 \ MPa)\,(40.64 \ cm)}{(2)\,(0.635 \ cm)} = 32 \ MPa$$

$$i = \frac{zF\rho B}{tA_{w,Fe}} = \frac{(2)\,(96,500 \ A.\sec/mol)\,(7.86 \ g/cm^3)\,(0.635 \ cm)}{(6.312 \times 10^8 \ \sec)\,(55.85 \ g/mol)}$$

$$i = 27.33 \ \mu A/cm^2$$

The current and the potential for protecting the steel tank are based on the lateral area of the tank in contact with water. Letting the water column be $h = 76.20 \ cm$ yields

$$A_s = A_o\,(1 - \lambda_s)$$
$$A_s = \pi D_i h\,(1 - \lambda_s) = (\pi)\,(40.64 \ cm)\,(76.20 \ cm)\,(1 - 0.98)$$
$$A_s = 194.58 \ cm^2$$
$$I = iA_s = \left(27.33 \ \mu A/cm^2\right)\left(194.58 \ cm^2\right) = 5.32 \ mA$$

The cell potential along with the NACE recommended potential of -0.85 $V_{Cu/C\,SO_4}$ is

$$E = E_c + E_a = 0.85 \ V + 1.5 \ V = 0.65 \ V$$

Thus, the system resistance is

$$R_s = \frac{E}{I} = \frac{0.65 \ V}{5.32 x 10^{-3} \ A} = 122.18 \ ohm$$

(c) *The anode lifetime is based on the oxidation reaction $Mg \rightarrow Mg^{+2} + 2e$. From eq. (8.4), the anode capacity is*

$$C_a = \frac{\epsilon z F}{A_w} = \frac{(0.50)\,(2)\,(96,500 \ A.s/mol)}{24.31 \ g/mol} = 1,103 \ A.h/Kg$$

Thus, anode effective length is $L_a = 0.75H = (0.75)\,(85 \ cm) = 63.75 \ cm$ so that the anode mass becomes

$$V_a = \frac{\pi d^2 L_a}{4} = \frac{(\pi)\,(5.08 \ cm)^2\,(63.75 \ cm)}{4} = 1,292.10 \ cm^3$$
$$m_a = \epsilon \rho_a V_a = (0.50)\,(1.74 \ g/cm^3)\,(1,292.10 \ cm^3)$$
$$m_a = 1.12 \ Kg$$

From Table 8.4, the average anode lifetime is

$$
\begin{aligned}
L_d &= \frac{7 C_a m_a}{3 \pi I_a} = \frac{(7)\,(1,103\ A.h/Kg)\,(1.12\ Kg)}{(3\pi)\,(5.32x10^{-3}\ A)} \\
L_d &= 172.468.11\ h = 19.7\ years
\end{aligned}
$$

This result seems reasonable.

(d) *A* 1.12 *Kg of anode mass will deliver an electric energy of*

$$
\begin{aligned}
E_E &= C_a m_a \\
E_E &= (1,103\ A.h/Kg)\,(1.12\ Kg) = 1,235.36\ A.h \\
E_E &= 4.45\ MJ
\end{aligned}
$$

Recall that $1\ J = 1\ A.s.$

ANODIC PROTECTION

8.8 For anodic protection, the interface potential of the structure is increased to passive domain, provided that the metal exhibits active-passive behavior. Thus, prevention of corrosion is through impressed anodic current. Explain including the mathematical definition of the applied anodic current density.

Explanation: *The impressed anodic current imparts an initial corrosion rate* (i_{corr}) *is shifted to a low value at* i_{pass} *(passive current density). Otherwise, passivation will not occur. The applied anodic currents density*

$$
i = i_{ox} - i_{red}
$$

where i_{ox} *is the oxidation and* i_{red} *is the reduction current densities.*

8.9 What are the implications of cathodic protection of steels in acid solutions?

Answer: *The cathodic protection currents in acid solution can lead to hydrogen liberation* (H_2) *and embrittlement of steels. This makes anodic protection the most preferred choice for protection of chemical process equipment.*

8.10 Why is passivation important for anodic protection? What is the mechanisms that explains the electron motion for reactions to take place?
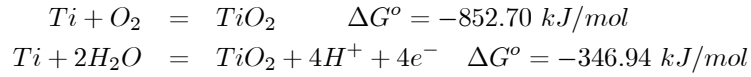
Answer: *First of all, passivation is the process for oxide film formation on the metal exposed to an acid solution. Once passivation is completed, an anodic current-potential pair has to be kept within a reasonable range to keep the metal*

in its passivated stated. The mechanism is quantum mechanical electron tunneling through a thin oxide film, which may be an insulator or a semiconductor. However, ionic tunneling seems to be restricted by the film width acting as a barrier.

8.11 What are the passive film preferred break-down sites?

Answer: *Grain boundaries (if any), nonmetallic inclusions and flaws on the metal oxide surface.*

8.12 Calculate (a) the potential for the two titanium reactions given below. These reactions represent the passivation process for titanium-oxide film formation. Thus, anodic protection is natural because the TiO_2 film acts as a semiconductor barrier to protect the underlying metallic Ti from corrosion, $Ti \rightarrow Ti^{2+} + 2e^-$ at $E^o = 1.63\ V_{SHE}$. (b) Determine the Ph.

$$
\begin{aligned}
Ti + O_2 &= TiO_2 & \Delta G^o &= -852.70\ kJ/mol \\
Ti + 2H_2O &= TiO_2 + 4H^+ + 4e^- & \Delta G^o &= -346.94\ kJ/mol
\end{aligned}
$$

Solutions:
(a) *The potential for* $Ti + O_2 = TiO_2$,

$$E = -\frac{\Delta G}{zF} = -\frac{(-852.70\ kJ/mol)}{2\,(96500\ J/mol.V)} = 4.42\ mV$$

Using the Nernst equation,

$$
\begin{aligned}
E &= E^o - \frac{RT}{zF} \ln K_{sp} = E^o - \frac{RT}{zF} \ln \frac{[TiO_2]}{[Ti]\,[O_2]} \\
E &= E^o \text{ since } [TiO_2] = [Ti] = [O_2] = 1
\end{aligned}
$$

For $Ti + 2H_2O = TiO_2 + 4H^+ + 4e^-$ *at* $E^o = -0.860\ V$ *(Table 2.3),*

$$E = -\frac{\Delta G}{zF} = -\frac{(-346.94\ kJ/mol)}{2\,(96500\ J/mol.V)} = 1.80\ mV$$

(b) *Using the Nernst equation for* $Ti + 2H_2O = TiO_2 + 4H^+ + 4e^-$ *gives the pH*

$$
\begin{aligned}
E &= E^o - \frac{RT}{zF} \ln K_{sp} = E^o - \frac{RT}{zF} \ln \frac{[TiO_2]\,[H^+]^4}{[Ti]\,[H_2O]^2} \\
E &= E^o - \frac{4RT}{zF} \ln [H^+] \quad \text{since } [TiO_2] = [Ti] = [H_2O] = 1
\end{aligned}
$$

Thus,

$$\left[H^+\right] = \exp\left[-\frac{zF\left(E-E^o\right)}{4RT}\right]$$

$$\left[H^+\right] = \exp\left[-\frac{2\left(96500\right)\left(0.0018+0.86\right)}{4\left(8.314\right)\left(298\right)}\right]$$

$$\left[H^+\right] = 5.1417 \times 10^{-8}$$

Then,

$$pH = -\log\left[H^+\right] = -\log\left(5.1417 \times 10^{-8}\right)$$

$$pH = 16.78$$

8.13 The effect of sulfuric acid (H_2SO_4) concentration on polarization behavior of a metal at 25^oC can be assessed obtaining experimental potentiodynamic polarization curves. Below is a data set for the critical current density (i_c) of a hypothetical metal.

C (%)	0	20	30	40	50	60	70
i_c (A/cm^2)	46	30	23	17	12	8	5

Plot $i_c = f\left(C\right)$ and explain whether or not passivation is affected by the concentration of sulfuric acid.

Solution:
Curve fitting yields a polynomial fit: $i_c = 46.096 - 0.907\,23C + 4.552\,3 \times 10^{-3}C^2$ *with* $R^2 = 0.98$. *The plot is*
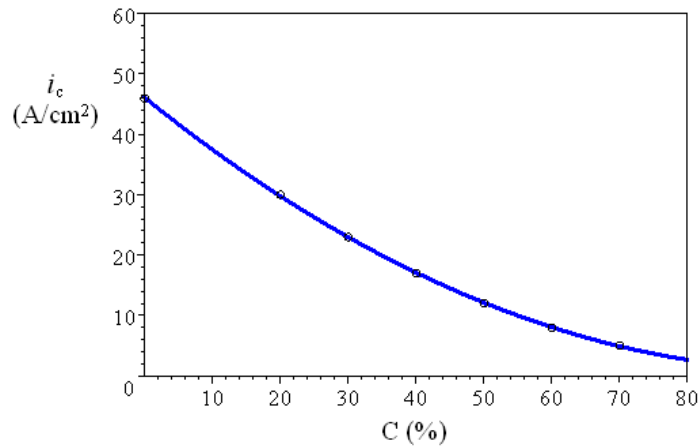
For anodic protection, i_c must exist for passivation to take place by the formation of an oxide film. The plotted data indicates that i_c nonlinearly decrease with increasing percent concentration. This trend means that passivation is readily as i_c decreases because at the applied current density $i = i_c \rightarrow i_{pass}$ until $E \rightarrow E_{pass} > E_{corr}$. Therefore, passivation is enhanced by increasing H_2SO_4 concentration.

8.14   Below is a data set taken from Table 12.7 in reference [10] for determining the effect of concentration of sulfuric acid (H_2SO_4) at 24°C on the critical current density of 316 (UNS S31600) stainless steel at 24°C.

$\%C_{H_2SO_4}$	0	40	45	55	65	75
$i_c \; (mA/cm^2)$	4.7	1.6	1.4	1.0	0.7	0.4
$C_{R.i_{corr}} \; (mm/y)$	0	2.2	5.6	8.9	7.8	6.7

(a) Do non-linear curve fitting on i_c versus $\%C_{H_2SO_4}$ and plot $i_c = f\left(\%C_{H_2SO_4}\right)$. **(b)** Assume that Fe, Cr, Mo and Mn oxides simulteneously go into solution. Now calculate C_R for these four elements using the given experimental i_c values, do curve fitting on the new C_R data set and the experimental $C_{R.i_{corr}}$ values versus $\%C_{H_2SO_4}$. Plot the C_R functions for Fe, Cr, Mo and Mn, and plot the experimental $C_{R.i_{corr}}$ data ant its linear curve fit equation in order to compare the corrosion behavior of the stainless steel at i_{corr} and these elements i_c. Explain.

Solution:

(a) Non-linear curve fitting. Let $y = i_c$ and $x = \%C_{H_2SO_4}$

$$i_c = 4.6924 - 9.8094 \times 10^{-2}C + 5.5224 \times 10^{-4}C^2$$

with a correlation coefficient $R^2 = -0.97$. The plot is
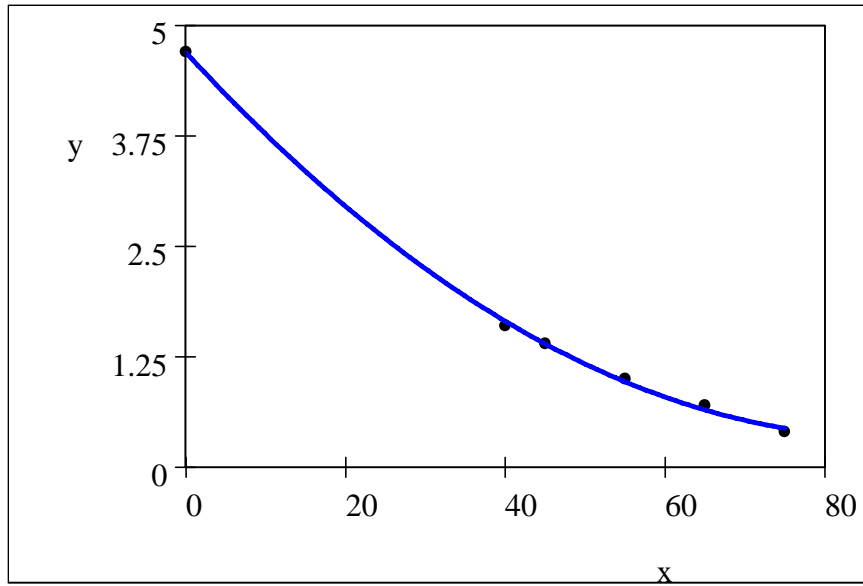
Actually, A_w has been used as the atomic weight of an element, but now A_w becomes the molecular weight of the alloy.

Element	Fe	C	Cr	Mn	Mo	Ni	Si	P	S
%	62	0.08	18	2	3	14	1	0.045	0.03

$$A_w = \frac{1}{100}\sum f_i A_{w,i} = \frac{1}{100}\left(62 * 55.845 + 0.08 * 12 + 18 * 51.996 + ...\right)$$
$$A_w = 75.684 g/cm^3$$

Oxidation of iron (Fe):
$A_{w,Fe} = 55.85\ g/mol$ $\qquad \rho_{Fe} = 7.857\ g/cm^3$ $\qquad Fe \rightarrow Fe^{2+} + 2e^-$ with $z = 2$

$$C_{R,Fe,i_c} = \frac{i_c A_{wFe}}{zF\rho_{Fe}} = \frac{(55.85\ g/mol)(i_c)}{(2)(96500\ A.s/mol)(7.857\ g/cm^3)}$$

$$C_{R_{Fe}} = \frac{i_c A_{wFe}}{zF\rho_{Fe}} = \frac{(55.85)(0.4)(10^{-3})}{(2)(96500)(7.857)}(10)(60*60*24*365) = 4.6460$$

$\%C_{H_2SO_4}$	0	40	45	55	65	75
$i_c\ (mA/cm^2)$	4.7	1.6	1.4	1.0	0.7	0.4
$C_{R,Fe.i_c}\ (mm/y)$	54.59	18.58	16.26	11.62	8.13	4.65

Polynomial fit: $y_{Fe} = 6.4166 \times 10^{-3}x^2 - 1.1395x + 54.501$ with $R^2 = -0.97$

Oxidation of chromium (Cr):

$$A_{w,Cr} = 52 \ g/mol \qquad \rho_{Cr} = 7.19 \ g/cm^3 \qquad Cr \rightarrow Cr^{3+} + 3e^- \ \text{with } z = 3$$

$$C_{R,Cr,i_c} = \frac{i_c A_{w_{Cr}}}{zF\rho_{Cr}} = \frac{(52 \ g/mol)\,(i_c)}{(3)\,(96500 \ A.s/mol)\,(7.19 \ g/cm^3)}$$

$$C_{R_{Fe}} = \frac{(52)(0.4)\left(10^{-3}\right)}{(3)(96500\ )(7.19)}\,(10)\,(60*60*24*365) = 3.1513$$

$\%C_{H_2SO_4}$	0	40	45	55	65	75
$i_c \ \left(mA/cm^2\right)$	4.7	1.6	1.4	1.0	0.7	0.4
$C_{R,Cr.i_c} \ (mm/y)$	37.03	12.61	11.03	7.88	5.51	3.15

Polynomial fit: $y_{Cr} = 4.5731 \times 10^{-3}x^2 - 0.772\,92x + 36.862$ with $R^2 = -96$

Oxidation of molybdenum (Mo):
$A_{w,Mo} = 95.96 \ g/mol \qquad \rho_{Mo} = 10.22 \ g/cm^3 \qquad Mo \rightarrow Mo^{3+} + 2e^-$ with $z = 3$

$$C_{R,Mo,i_c} = \frac{i_c A_{w_{Mo}}}{zF\rho_{Mo}} = \frac{(95.96 \ g/mol)\,(i_c)}{(3)\,(96500 \ A.s/mol)\,(10.22 \ g/cm^3)}$$

$$C_{R_{Fe}} = \frac{(95.96)(0.4)\left(10^{-3}\right)}{(3)(96500\ )(10.22)}\,(10)\,(60*60*24*365) = 4.0913$$

$\%C_{H_2SO_4}$	0	40	45	55	65	75
$i_c \ \left(mA/cm^2\right)$	4.7	1.6	1.4	1.0	0.7	0.4
$C_{R,Mo.i_c} \ (mm/y)$	48.07	16.37	14.32	10.23	7.16	4.09

Polynomial fit: $y_{Mo} = 5.3368 \times 10^{-3}x^2 - 0.967\,2x + 47.000$ with $R^2 = -0.98$

Oxidation of manganese (Mn):
$A_{w,Mn} = 54.94 \qquad \rho_{Mn} = 7.44 \ g/cm^3 \qquad Mn \rightarrow Mn^{2+} + 2e^-$ with $z = 2$

$$C_{R,Mn,i_c} = \frac{i_c A_{w_{Mn}}}{zF\rho_{Mn}} = \frac{(54.94 \ g/mol)\,(i_c)}{(2)\,(96500 \ A.s/mol)\,(10.22 \ g/cm^3)}$$

$$C_{R_{Fe}} = \frac{(54.94)(0.4)\left(10^{-3}\right)}{(2)(96500\ )(7.44)}\,(10)\,(60*60*24*365) = 4.8264$$

$\%C_{H_2SO_4}$	0	40	45	55	65	75
$i_c \ \left(mA/cm^2\right)$	4.7	1.6	1.4	1.0	0.7	0.4
$C_{R,Mn.i_c} \ (mm/y)$	56.71	19.31	16.89	12.07	8.45	4.83

Plots: $y = C_{R,i_c}$ and $x = \%C_{H_2SO_4}$. Red dot are experimental data from the i_{corr} point of the polarization curves. So $i_c > i_{corr}$ at $C_{H_2SO_4} < 55\%$.
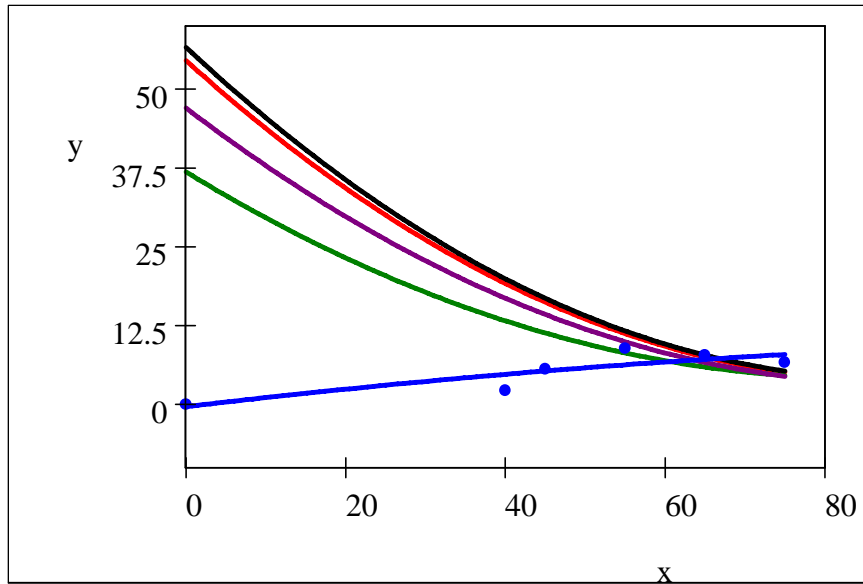Red (2): $\qquad y_{Fe} = 6.4166 \times 10^{-3}x^2 - 1.1395x + 54.501$
Green (4): $\quad y_{Cr} = 4.5731 \times 10^{-3}x^2 - 0.772\,92x + 36.862$
Purple (3): $y_{Mo} = 5.3368 \times 10^{-3}x^2 - 0.967\,2x + 47.000$
Black (1 Top Curve): $\quad y_{Mn} = 6.\,6637 \times 10^{-3}x^2 - 1.1836x + 56.618$
Experimental: $y_{C_R,\exp} = 0.148\,87x - 5.1658 \times 10^{-4}x^2 - 0.32656$
$\qquad\qquad$ with $R^2 = 0.85$

The above figure shows that the AISI 316 stainless steel is a corrosion resistant alloy, but the curves for Fe, Cr, Mo and Mn indicate that these elements oxide very rapidly at $C_{H_2SO_4} < 55\%$. Beyond this concentration the experimental data and the calculated C_R values are similar. In other words, when $C_{H_2SO_4} \geq 55\%$ the i_{corr} and i_c position on the polarization curves are not far apart on the normal log scale (x-axis).

8.15 This problem deals with the nature of the anodic oxide film that forms on titanium in 0.9% $NaCl$. This media is isotonic with human blood for surgical implants made out of titanium and its alloys. Normally, the passive oxide film on titanium mainly consists of TiO_2. The table given below contains data for the passive current density (i_p) as a function of sweep rate (de/dt in mV/s) [52] on titanium in 0.9% $NaCl$ containing electrolyte. **(a)** Convert the i_p data to corrosion rate C_R in mm/y. Then plot both i_p and C_R as functions of sweep rate $v = dE/dt$. **(b)** Explain if this titanium material would be suitable for a human transplant for a prolong time.

$v = dE/dt \ (mV/s)$	10	50	100	300	500
$i_p \ (mA/cm^2)$	0.13	0.25	0.50	1.58	2.10

Solution:

The oxidation reaction for titanium is $Ti \rightarrow Ti^{2+} + 2e^-$ @ $E^o = 1.630 \ V_{SHE}$. The corrosion rate is

$$C_R = \frac{i_p A_w}{zF\rho}$$
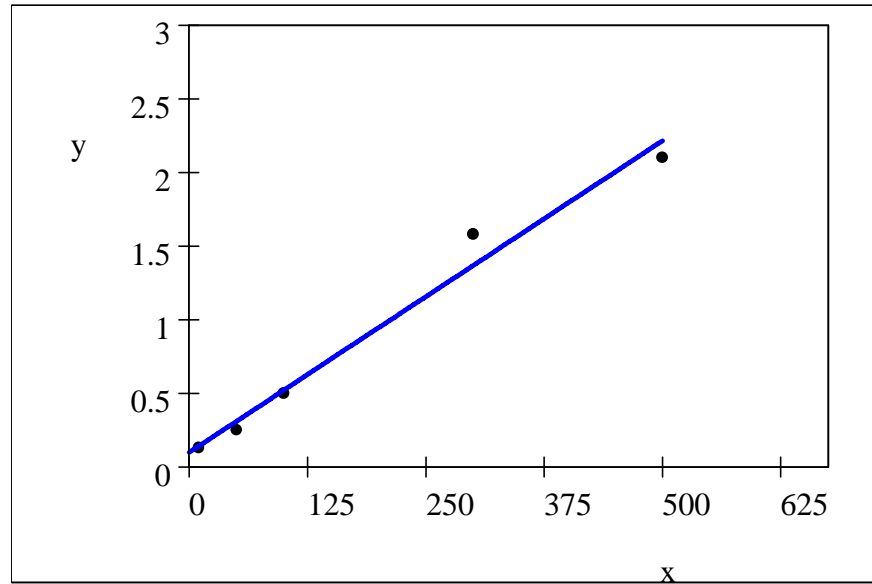
For $A_w = 47.867 \ g/mol$ and $\rho = 4.54 \ g/cm^3$,

$$\frac{A_w}{zF\rho} = \frac{47.867 \text{ g/mol}}{(2)(96500 \text{ A.s/mol})\left(4.54 \text{ g/cm}^3\right)} = 5.4629 \times 10^{-5} \ \frac{cm^3}{A.s}$$

Thus,

$$C_R = \left(5.4629 \times 10^{-5} \ \frac{cm^3}{A.s}\right) i_p$$

$v = dE/dt \ (mV/s)$	10	50	100	300	500
$i_p \ (mA/cm^2)$	0.13	0.25	0.50	1.58	2.10
$C_R \ (\times 10^{-8} \ mm/y)$	7.10	13.66	27.32	86.31	114.72

Let $y = i_p$ and $x = v$. The plot for $i_p = f(v)$ is

Curve fitting gives

$$i_p = \left(0.09932 \ \frac{mA}{cm^2}\right) + \left(4.2327 \times 10^{-3} \ \frac{mA}{cm^2} \frac{s}{mV}\right) v$$

with a correlation coefficient $R^2 = 0.99$.

Let $y = C_R$ and $x = v$. The plot for $C_R = f(v)$ is

$$
\begin{array}{llllll}
v = dE/dt \ (mV/s) & 10 & 50 & 100 & 300 & 500 \\
i_p \ (mA/cm^2) & 0.13 & 0.25 & 0.50 & 1.58 & 2.10 \\
C_R \ (\times 10^{-8} \ mm/y) & 7.10 & 13.66 & 27.32 & 86.31 & 114.72
\end{array}
$$

Polynomial fit: $y = (0.23122x + 5.4276) \left(10^{-8} \ mm/y\right)$ with a correlation coefficient $R^2 = 0.99$
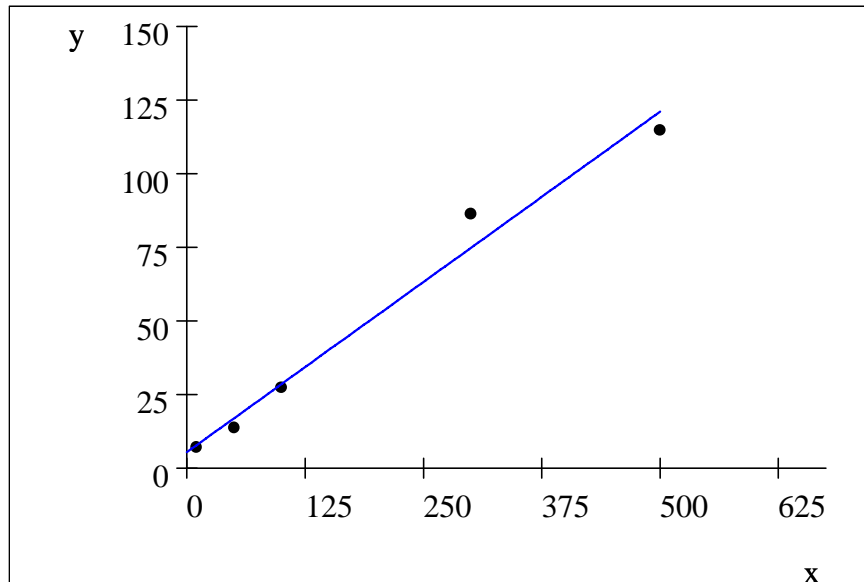
These results indicate that a titanium transplant is suitable for a human being. For instance, the lowest and highest corrosion rates are

$$
\begin{aligned}
C_{R,\min} &= (0.23122\,(10) + 5.4276)\left(10^{-8}\right) = 7.74 \times 10^{-8} mm/y \\
C_{R,\max} &= (0.23122\,(500) + 5.4276)\left(10^{-8}\right) = 1.21 \times 10^{-6} mm/y
\end{aligned}
$$

The corrosion rates are extremely low and therefore, the titanium transplant would not cause detrimental health effects in humans.

Chapter 9

ELECTRODEPOSITION

9.1 PROBLEMS

9.1 Copper cations are reduced on a cathode for 8 *hours* at a current of 10 *amps.* and 25^oC. Calculate a) the theoretical weight of copper deposited on the cathode and b) the number of coulombs of electricity in this electrodeposition process. Data: $A_{w,Cu} = 63.55$ g/mol and $F = 96,500$ C.

Solution:

$$Cu^{+2} + 2e = Cu$$
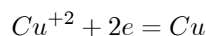
a) *From eq.* (9.8g) *with* $F = 96,500$ $C = 96,500$ $A.s/mol$

$$W = \frac{ItA_w}{zF} = \frac{(10\ A)\,(8x60x60\ s)\,(63.55\ g/mol)}{(2)\,(96,500\ A.s/mol)}$$
$$W = 94.83\ grams \quad @ \quad 100\%\ efficiency$$

b) *From eq.* (9.8b),

$$Q = It = (10\ A)\,(8x60x60\ s)$$
$$Q = 288,000\ C\ (= A.s)$$

9.2 An electrochemical cell operates at 6 A, 25^oC and 85% current efficiency in order to electrolytically deposit copper ions (Cu^{+2}) from a leaching solution in a $8 - hour$ shift. Calculate a) the amount of electrolytically deposited Cu and b) the thickness of the deposit layer of copper. Data: $A_s = 100$ cm^2 (total cathode surface area), $A_{w,Cu} = 63.55$ g/mol, $\rho = 8.96$ g/cm^3 and $F = 96,500$ C/mol.

Solutions:

$$Cu^{+2} + 2e = Cu$$
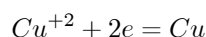
a) *From eq. (9.9) with $F = 96,500\ C = 96,500\ A.s/mol$*

$$W = \frac{\epsilon I t A_w}{zF} = \frac{(0.85)\,(6\ A)\,(8x60x60\ s)\,(63.55\ g/mol)}{(2)\,(96,500\ A.s/mol)}$$

$$W = 48.36\ grams$$

b) *Letting $m = W = 48.36\ grams$ yields*

$$V = xA_T = \frac{m}{\rho}$$

$$x = \frac{m}{\rho A_T} = \frac{48.36\ g}{(8.96\ g/cm^3)\,(100\ cm^2)}$$

$$x = 0.54\ mm$$

9.3   It is desired to electroplate chromium (Cr) onto a ferritic-martensitic carbon steel automobile bumper for an attractive appearance and corrosion resistance. An electroplating cell is operated at $I = 6.68\ A$ and $25^{o}C$. The Cr^{+3} cations are reduced on the bumper (cathode) to form a thin film of $1.5\ \mu m$ thick. How long will it take to produce a $1.5\ \mu m$ thick electroplated chromium film on the bumper if the total surface area is $100\ cm^2$ and $\epsilon = 60\%$?

Solution:

$$Cr^{+3} + 3e = Cr$$
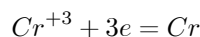
a) *Using eq. (9.9) with $F = 96,500\ C = 96,500\ A.s/mol, \rho = 7.20\ g/cm^3$ and $A_w = 52\ g/mol$ yields*

$$W = \frac{\epsilon I t A_w}{zF} = \frac{(0.85)\,(6\ A)\,(8x60x60\ s)\,(63.55\ g/mol)}{(2)\,(96,500\ A.s/mol)}$$

$$W = V\rho = A_s x\rho = (100\ cm^2)\,(1.5x10^{-4}\ cm)\,(7.20\ g/cm^3)$$

$$W = 0.1080\ g$$

$$t = \frac{zFW}{\epsilon I A_w} = \frac{(2)\,(96,500\ A.s/mol)\,(0.1080\ g)}{(0.60)\,(6.68\ A)\,(52\ g/mol)}$$

$$t = 100\ sec$$

9.4   An electrowinning cell contains $2x10^{-4}\ mol/cm^3$ of Cu^{+2} ions and operates for 10 minutes at $40^{o}C$ and $1\ atm$. Assume an ionic copper diffusivity equals to $2.34x10^{-5}\ cm^2/s$. Calculate the current density due to diffusion mass transfer. Compare your result with a typical industrial current density value of $200\ A/m^2$. Explain any discrepancy.

Solution:

$$Cu^{+2} + 2e = Cu$$
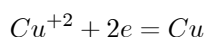
From eq. (9.68),

$$J_d = \frac{DC_o}{\sqrt{\pi Dt}} = C_o\sqrt{\frac{D}{\pi t}}$$

$$J_d = \left(2x10^{-4}mol/cm^3\right)\sqrt{\frac{\left(2.34x10^{-5}cm^2/s\right)}{(\pi)(600\ s)}}$$

$$J_d = 2.23x10^{-8}\ \frac{mol}{cm^2.s}$$

From eq. (9.71),

$$i_d = zFJ_d = (2)(96,500\ A.s/mol)\left(2.23x10^{-8}\ \frac{mol}{cm^2.s}\right)$$

$$i_d = 4.30x10^{-3}\ A/cm^2 \simeq 43\ A/m^2$$

Obviously, the assume diffusion mechanism for reducing copper ions is just part of the total mass transfer. In fact, $i_d = 43\ A/m^2$ represents approximately 22% of the total current density. If the electrolyte is continuously replenished with fresh electrolyte, then the remaining 78% current density has to come from migration and convection mass transfer.

*The total molar flux using $200\ A/m^2$ current density is*

$$J_x = \frac{i}{zF} = \frac{200x10^{-4}\ A/cm^2}{(2)(96,500\ A.s/mol)}$$

$$J_x = 1.04x10^{-7}\ \frac{mol}{cm^2.s}$$

Thus, the migration and convection molar flux becomes

$$J_m + J_c = J_x - J_d = 8.13x10^{-8}\ \frac{mol}{cm^2.s}$$

9.5 Calculate the amount of silver that can be electroplated in an electrochemical cell containing Ag^+ ions and operates at 7 A, 25^oC and 101 kPa for 10 minutes. Assume a current efficiency of 95%.

Solution:

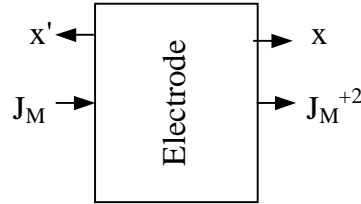$$Ag^+ + e = Ag$$
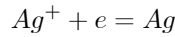
From eq. (9.9),

$$W = \frac{\epsilon It A_w}{zF} = \frac{(0.95)(7\ A)(10x60\ s)(107.87\ g/mol)}{(1)(96,500\ A.s/mol)}$$

$$W = 4.46\ grams$$

9.6 What are the differences between galvanic and electrolytic cells? Recall that both are electrochemical cells.

Answer: *Figure 2.2 shows the differences between these cells. However, in a galvanic cell, a chemical reaction generates an electric current flow and consequently,chemical energy is converted into electrical energy and the cathode is the positive electrode. On the other hand, in an electrolytic cell, electrical energy is converted into chemical energy and the cathode is the negative electrode since the supply of electrons comes from an external source, such as a galvanic cell or dc generator.*

9.7 Consider the bipolar electrode for electrorefining metal M. Thus, the rate of formation (reduction) and dissolution (oxidation) are treated as steady-state quantities. Despite that the initial formation of a thin film at the cathode face and dissolution rates are controlled by reactions at the electrode-electrolyte interfaces, assume a steady-state diffusion mechanism. Derive expressions for the weight gain at the cathode side and the weight loss at the anode side.

Solution:

Reduction	Oxidation
$J_M = -D\partial C/\partial x'$	$J_{M^{+2}} = -D\partial C/\partial x$
$J_M = -D'\left(C'_o - C_{x'}\right)/x'$	$J_{M^{+2}} = -D\left(C'_x - C_o\right)/x$
$C_o > C_{x'}$	$C_x > C_o$
$W' = V'\rho' = x'A'\rho'$	$W = V\rho = xA\rho$

Eliminating x' and x yields

$$W' = A'\rho'D'\left(C'_o - C_{x'}\right)/J_M \qquad W = A\rho D\left(C'_x - C_o\right)/J_{M^{+2}}$$

According to the given conditions, $W' = W$ since $A' = A$, $\rho' = \rho$ and $J_M = J_{M+2}$.

9.8 A steel plate is Ni-plated for corrosion protection, but its appearance is not so appealing. Therefore, a chromium electroplating process is carried out for decorative purposes. Eventually, $0.25\ g$ of Cr^{+6} cations are electroplated on the

Ni-plated surface for a period of 15 minutes at 8 *amps*. If the density and atomic weight of chromium are 7.19 g/cm^3 and 52 g/mol, respectively, calculate **(a)** the thickness of the electroplated film of chromium from its highest oxidation state and **(b)** the deposition rate. Data: $A_s = 100 \ cm^2$ (cathode area).

Solution:

$$Cr^{+6} + 6e^- \overset{H^+}{=} Cr$$
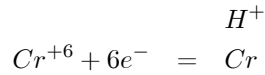
(a) *Thickness*:

$$x = \frac{W}{A_s \rho} = \frac{0.25 \ g}{(100 \ cm^2)(7.19 \ g/cm^3)}$$
$$x = 3.48 \ \mu m$$

(b) *Production rate*:

$$P_R = \frac{W}{t} = \frac{0.25 \ g}{900 \ s} = 2.78x10^{-4} \ g/s$$
$$P_R = 1 \ g/h$$

(c) *From eq. (9.16)*,

$$\epsilon = \frac{zFW}{ItA_w}$$
$$\epsilon = \frac{(6)\left(96{,}500 \ \frac{A.s}{mol}\right)(0.25 \ g)}{(8 \ A)(900 \ s)(52 \ g/mol)} = 0.39$$
$$\epsilon = 39\%$$

This is a low, but typical current efficiency in Cr electroplating.

9.9 It is desired to produce a 20 μm thick film of chromium on a Ni-plated steel part, which has a surface area of 65 cm^2. This can be accomplished by setting up an electroplating cell to operate at 7 *amps* and current efficiency of 70%. The density and atomic weight of chromium are 7.19 g/cm^3 and 52 g/mol, respectively. Calculate a) the amount of Cr being plated and b) the time it takes to plate the 20 μm thick film of chromium from a solution containing Cr^{+6} cations at 30^oC.
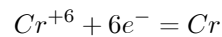
Solution:

$$Cr^{+6} + 6e^- = Cr$$

a) *Amount of Cr*:

$$W = V\rho = \rho x A_s$$
$$W = \left(7.19 \ g/cm^3\right)\left(20x10^{-4} \ cm\right)\left(65 \ cm^2\right)$$
$$W = 0.94 \ g$$

b) *From eq. (9.16),*

$$t = \frac{zFW}{\epsilon I A_w}$$

$$t = \frac{(6)\left(96,500\ \frac{A.s}{mol}\right)(0.94\ g)}{(0.70)(7\ A)(52\ g/mol)} = 2,124.67\ \text{sec}$$

$$t = 35.40\ \text{min}$$

9.10 Predict **(a)** the electric potential E, **(b)** the time in minutes, and **(c)** the film growth rate in $\mu m/\min$ for electroplating a 10 μm-thick Cr film on a Ni-undercoated steel part when the electrolyte contains 10^{-4} mol/l of Cr^{+3} cations at 25^oC. The Ni-plated steel part has a 10 cm^2 surface area. The cell operates at 50% current efficiency and at a passive current density of $5.12x10^{-3}$ A/cm^2.

Solution:

$Cr^{+3} + 3e = Cr$ $E^o_{Cr} = -0.744\ V$ $z = 3$
$\rho = 7.19\ g/cm^3$ $A_{w,Cr} = 52\ g/mol$
$A_s = 10\ cm^2$ $\epsilon = 0.50$ $a_{Cr^{+3}} = 10^{-4}\ mol/l$

(a) *Using Nernst equation yields*

$$E > E_o = E^o + \frac{RT}{zF} \ln\left(a_{Cr^{+3}}\right)$$

$$E > E_o = -.0744V + \frac{(8.314\ J/mol.K)(298\ K)}{(3)(96,500\ J/mol.V)} \ln\left(10^{-4}\right)$$

$$E > E_o = -0.82\ V$$

(b) *Integrating eq. (7.21) yields the time*

$$t = \int_0^x \left(\frac{zF\rho}{\epsilon i A_w}\right) dx = \frac{zF\rho x}{\epsilon i A_w}$$

$$t = \frac{(3)(96,500\ A.s/mol)\left(7.19\ g/cm^3\right)\left(10^{-4}\ cm\right)}{(0.50)\left(5.12x10^{-3}\ A/cm^2\right)(52\ g/mol)}$$

$$t = 26\ \text{min}$$

(c) T*he film growth rate is*

$$\frac{dx}{dt} = \frac{\Delta x}{\Delta t} = \frac{10\ \mu m}{26\ min}$$

$$\frac{dx}{dt} = 0.38\ \frac{\mu m}{min}$$

9.11 The dissociation of silver hydroxide, $AgOH$, is $1.10x10^{-4}$ at $25\,°C$ in an aqueous solution. (a) Derive an expression for the degree of dissociation as a function of total activity $[C_T]$ and plot the resultant expression for $0 < [C_T] < 0.50\ mol/l$, (b) calculate the degree of dissociation constant α_1 when the molar concentration is $[C_T] = 0.144\ mol/l$, and (c) determine the Gibbs free energy change ΔG^o.
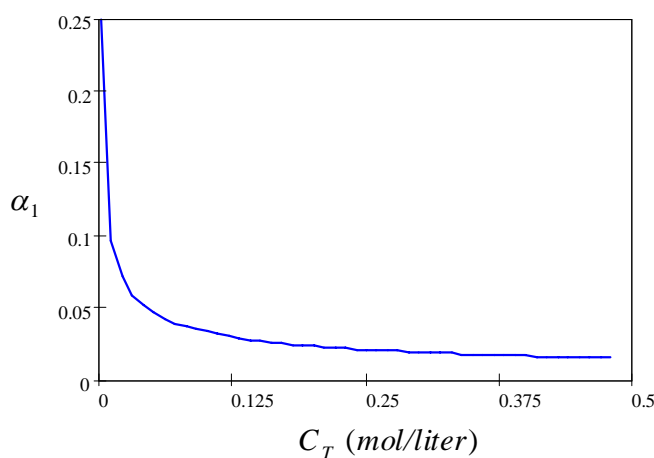
Solution:

a) *The expression and the plot are*

$$AgOH = Ag^+ + OH^-$$
$$K_e = \frac{[Ag^+][OH^-]}{[AgOH^-]} = 1.10x10^{-4}$$

From eq. (2.67) with $x = y = 1$,

$$\alpha_1 = \left(K_e x^{-x} y^{-y}\right)^{1/(x+y)} [C_T]^{-1+1/(x+y)} = K_e^{1/2} [C_T]^{-1/2}$$
$$\alpha_1 = \left(1.05x10^{-2}\right) [C_T]^{-1/2}$$

C_T *(mol/liter)*

b) *The degree of dissociation:*

$$\alpha_1 = \left(1.05x10^{-2}\right) [0.144]^{-1/2} = 0.028$$

c) *The free energy change is*

$$\Delta G^o \;=\; -RT \ln(K_e) = - \left(8.314 \; \frac{J}{mol.^oK} \right) (298^oK) \ln\left(1.1x10^{-4}\right)$$

$$\Delta G^o \;\approx\; -22.58 \; kJ/mol$$

Therefore, the reaction as written will proceed since $\Delta G^o < 0$.

9.12   Calculate (a) the concentration of $AgOH$, Ag^+ and OH^- at $25\,^\circ C$ and (b) the pH if $[C_T] = 0.144 \; mol/l$ and $\alpha_1 = 0.028$.

Solution:

a) $AgOH = Ag^+ + OH^-$ *and* $K = 1.10x10^{-4}$ *(From Example 2.11). Let* $[Ag^+] = [OH^-]$ *for charge balance so that*

$$K_e \;=\; \frac{[Ag^+][OH^-]}{[AgOH]} = \frac{[OH^-]^2}{[AgOH]} \tag{a}$$

$$[OH^-] \;=\; \sqrt{K[AgOH]} \tag{b}$$

The dissociation of water ant its rate constant are

$$H_2O \;=\; H^+ + OH^- \tag{c}$$

$$K_w \;=\; \frac{[H^+][OH^-]}{[H_2O]} = 10^{-14} \tag{d}$$

From eq. (2.64a) along with $[H_2O] = 1 \; mol/l$,

$$[OH^-] \;=\; x\alpha_1[C_T] = (1)(0.028)[0.144 \; mol/l] = 4.03x10^{-3} \; mol/l \tag{e}$$

$$C_{OH^-} \;=\; [OH^-]\,A_{w,OH} = \left(4.03x10^{-3}\,\frac{mol}{l}\right)\left(17\,\frac{g}{mol}\right) = 6.85x10^{-2}\,\frac{g}{l} \tag{f}$$

$$[Ag^+] \;=\; [OH^-] = 4.03x10^{-3} \; mol/l \tag{g}$$

$$C_{Ag^+} \;=\; [Ag^+]\,A_{w,Ag} = \left(4.03x10^{-3}\,\frac{mol}{l}\right)\left(107.87\,\frac{g}{l}\right) = 0.43\,\frac{g}{l} \tag{h}$$

From eq. (2.64c),

$$[AgOH] \;=\; (1-\alpha_1)[C_T] = 0.14 \; mol/l$$

$$C_{AgOH} \;=\; [AgOH]\,A_{w,[AgOH]} = (0.14 \; mol/l)\,(124.87 \; g/mol)$$

$$C_{AgOH} \;=\; 17.48 \; g/l$$

From eq. (d),

$$\left[H^+\right] = \frac{K_w}{\left[OH^-\right]} = \frac{10^{-14}}{4.03x10^{-3}\ mol/l} = 2.48x10^{-12}\ mol/l$$

$$pH = -\log\left[H^+\right] = -\log\left(2.48x10^{-12}\right) = 11.61$$

9.13 An electrochemical cell contains 75 g/l of Cu^{+2} ions at 35^oC. Calculate (a) the Reynold and Sherwood numbers,(b) the diffusion flux (J_x), (c) the current density (i) and (d) the the applied potential (E). Data:

d	Characteristic distance	$= 12\ cm$	.
$L = x$	Cathode height	$= 100\ cm$	.
w	Cathode width	$= 80\ cm$	.
N	Number of cathodes	$= 50$	.
K_v	Kinematic viscosity	$= 0.80\ cm^2/s$	.
D	diffusivity	$= 1.24x10^{-5}\ cm^2/s$	
v_x	Flow velocity	$= 46.90\ cm/s$	.
P	Electrical Power	$= 32\ kW$	.

Solution:

$$Cu^{+2} + 2e = Cu \quad z = 2$$
$$C_{Cu^{+2}} = (75g/l)/(63.55\ g/mol) = 1.18\ mol/$$
$$C_{Cu^{+2}} = 1.18x10^{-3}\ mol/cm^3$$
$$\epsilon = 0.85 \qquad\qquad F = 96,500\ Aa.s/mol$$

(a) *From* eq. (9.4), (7.5) *and* (7.25), *the Reynold and Sherwood numbers are*

$$R_e = \frac{v_x d}{K_v} = \frac{(46.90\ cm/s)(12\ cm)}{(0.80\ cm^2/s)} = 703.50$$

$$S_c = \frac{K_v}{D} = \frac{0.80\ cm^2/s}{1.24x10^{-5}\ cm^2/s} = 64,516.13$$

$$S_h = \frac{2}{3}(S_c)^{1/3}(R_e)^{1/2} = 709.19$$

(b) *The diffusion flux* J_x:

$$J_x = -D\frac{\partial C}{\partial x} = -\frac{DC_{Cu^{+2}}}{x} =$$

$$J_x = \frac{\left(1.24x10^{-5}\ cm^2/s\right)\left(1.18x10^{-3}\ mol/cm^3\right)}{100\ cm}$$

$$J_x = 1.46x10^{-10}\ \frac{mol}{cm^2.s}$$

(c) *From* (7.13), *the current density is*

$$i = zFJ_xS_h$$

$$i = (2)\left(96,500\ \frac{A.s}{mol}\right)\left(1.46x10^{-10}\ \frac{mol}{cm^2.s}\right)(709.19)$$

$$i = 2x10^{-2}\ A/cm^2 = 200\ A/m^2$$

(d) *From elementary physics, the electrical power divided by the current is the applied potential. Thus,*

$$A_c = wL = (80\ cm)(100\ cm) = 8,000\ cm^2$$

$$A_s = 2NA_c = (2)(50)\left(8,000\ cm^2\right)$$

$$A_s = 800,000\ cm^2 = 80\ m^2$$

$$I = iA_s = \left(200\ A/m^2\right)\left(80\ m^2\right) = 16\ kA$$

$$E = \frac{P}{I} = \frac{32\ kW}{16\ kA} = \frac{32\ kV/A}{16\ kA}$$

$$E = 2\ volts$$

9.14 An electrolyte containing Pb^{+2} ions at 35^oC is used in an electrowinning cell. The electrolyte is under steady laminar force convection. Use the data given below to determine (a) the the Sherwood number, (b) the diffusion flux and (c) the current.

C_b	Bulk concentration	$= 75\ g/l$.
D	diffusivity	$= 1.24x10^{-5}\ cm^2/s$
$L = x$	Cathode length	$= 100\ cm$
S_c	Schmidt Number	$= 64,516.13$.
R_e	Reynolds Number	$= 703.50$.
A_s	Total cathode area	$= 800,000\ cm^2$
ϵ	Current efficiency	$= 85\%$

Solution:

$$Pb^{+2} + 2e = Pb$$

$$C_b = (75\ g/l)/(207.19\ g/mol)$$

$$C_b = 0.362\ mol/l = 3.62x10^{-4}\ mol/cm^3$$

(a) *From* eq. (9.25), *the Sherwood number is*

$$S_h = \frac{2}{3}(S_c)^{1/3}(R_e)^{1/2}$$

$$S_h = \frac{2}{3}(64,516.13)^{1/3}(703.50)^{1/2} = 709.19$$

(b) *The diffusion flux is*

$$J_x = -D\frac{\partial C}{\partial x} = -\frac{DC_b}{x} =$$

$$J_x = \frac{\left(1.24x10^{-5}\ cm^2/s\right)\left(3.62x10^{-4}\ mol/cm^3\right)}{100\ cm}$$

$$J_x = 4.49x10^{-11}\ \frac{mol}{cm^2.s}$$

(c) *The current is*

$$i = zFJ_xS_h$$

$$i = (2)\left(96,500\ \frac{A.s}{mol}\right)\left(4.49x10^{-11}\ \frac{mol}{cm^2.s}\right)(709.19)$$

$$i = 6.14x10^{-3}\ A/cm^2$$

$$I = iA_s = \left(6.14x10^{-3}\ A/cm^2\right)\left(800,000\ cm^2\right)$$

$$I = 4.91\ kA$$

9.15 A hypothetical rotating-disk cell is shown below for electrowinning copper cations from a solution containing $C_o = 65\ g/l$ at 40^oC and $101\ kPa$. Assume that the diffusivity and the electrolyte kinematic viscosity are 10^{-5} cm^2/s and $0.60\ cm^2/s$, respectively. Each disk has a radius of $50\ cm$, a width of $6\ cm$, and only a 160° segment is immersed in the electrolyte. Assume a cell current efficiency range of $0.50 \leq \epsilon \leq 1$.

Segment (S)
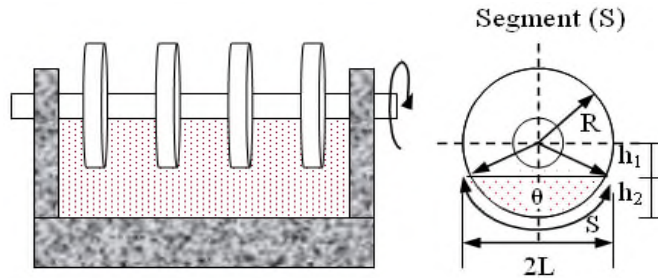
Theoretically, analyze the effect of a) the angular velocity ω on the current density and b) the angular velocity (ω) and the current density (ϵ) on the production rate of metal powder, and c) the potential (E) and the current density (ϵ) on the energy consumption γ.

Solution:

Data: $Cu^{+2} + 2e = Cu$ @ $T = 40^oC$

$C_o = 65 \ g/l = \left(65x10^{-3} \ g/l\right) / \left(63.55 \ g/mol\right)$	$A_w = 63.55 \ g/mol$
$C_o = 1.02x10^{-3} \ mol/cm^3$	$r = 50 \ cm$
$D = 10^{-5} \ cm^2/s$	$K_v = 0.60 \ cm^2/s$
$\theta = 160^o$	$w = 6 \ cm$

Total effective surface area:

$h_1 = r \cos\left(\theta/2\right) = 8.68 \ cm$	$L = r \sin\left(\theta/2\right) = 49.24 \ cm$
$h_2 = r = h_1 = 41.32 \ cm$	$S = \pi r \theta^o/180^o = 139.63 \ cm$
$A_{seg} = \frac{r^2}{2}\left(\frac{\pi\theta^o}{180^o}\right)$	

$$A_{seg} = \frac{r^2}{2}\left(\frac{\pi\theta^o}{180^o} - \sin\left(\theta\right)\right) = 3,063.13 \ cm^2$$
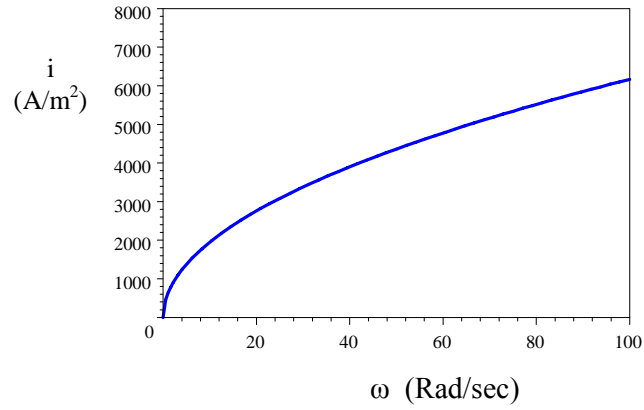
$$A_{arc} = wL = 295.44 \ cm^2$$

$$A_s = 4\left(2A_{seg} + A_{arc}\right) = 25,686.80 \ cm^2 \simeq 2.57 \ m^2$$

a) *From* eq. (9.107),

$$i = \frac{0.62zFC_oD^{2/3}\sqrt{\omega}}{K^{1/6}}$$

$$i = \frac{(0.62)(2)(96,500 \ A.s/mol)\left(1.02x10^{-3} \ mol/cm^3\right)\left(10^{-5} \ cm^2/s\right)^{2/3}\sqrt{\omega}}{\left(0.60 \ cm^2/s\right)^{1/6}}$$

$$i = \left(616.87 \ \frac{A.s^{1/2}}{m^2}\right)\sqrt{\omega}$$
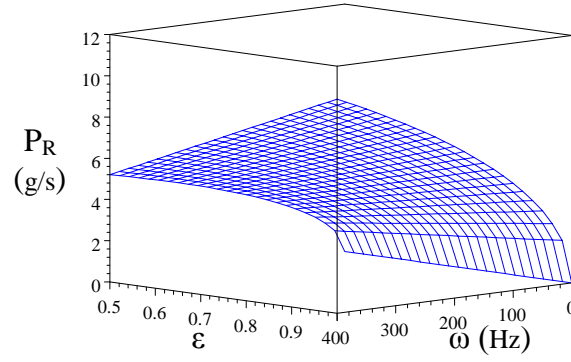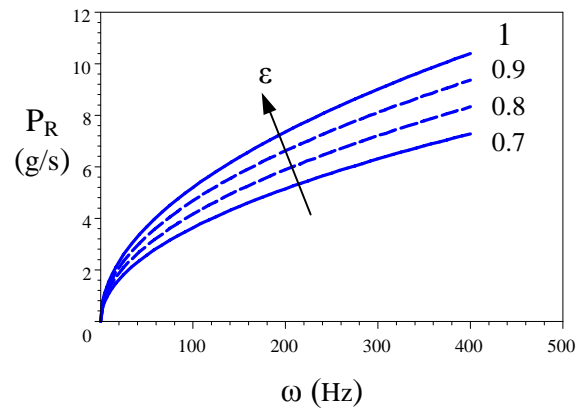
Figure 9.1:
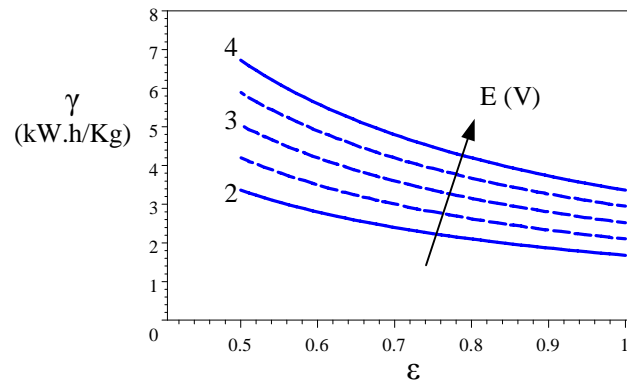
b) *From* 7.16,

$$P_R = \frac{\epsilon i A_s A_w}{zF} = \frac{\left(616.87 \; \frac{A.s^{1/2}}{m^2}\right) A_s A_w \epsilon \sqrt{\omega}}{zF}$$

$$P_R = \frac{\left(616.87 \; \frac{A.s^{1/2}}{m^2}\right)\left(2.57 \; m^2\right)\left(63.55 \; g/mol\right)\epsilon\sqrt{\omega}}{(2)\left(96,500 \; A.s/mol\right)}$$

$$P_R = \left(0.52 \; g.s^{1/2}/s\right)\epsilon\sqrt{\omega}$$

c) *From* eq. (9.18),

$$\gamma = \frac{zF}{A_w}\frac{E}{\epsilon}$$

$$\gamma = \frac{(2)\,(96,500\ A.s/mol)}{(63.55\ g/mol)}\frac{E}{\epsilon}$$

$$\gamma = \left(3,036.98\ \frac{A.s}{g}\right)\frac{E}{\epsilon}$$

$$\gamma = \left(0.84\ \frac{kW.h}{Kg}\right)\frac{E}{\epsilon} \quad \text{where } E \text{ is in volts}$$

The energy consumption does not depend directly on the angular velocity, but on the applied potential and current density, which in turn, depends on the applied current density.

9.16 Use the hypothetical rotating-disk voltammetry data given in the table below for determining the diffusivity D of a metal cation M^{+2} in solution at room temperature.

$\omega\ (1/\sec)$	100	225	400	625	900	1,225
$\omega^{1/2}\ \left(s^{1/2}\right)$	10	15	20	25	30	35
$i\ \left(mA/cm^2\right)$	4.81	7.22	9.58	12.10	14.38	16.80

$C_o = 2.21x10^{-6}\ mol/cm^3$
$K_v = 0.056\ cm^2/s$
$z = 2$

Solution:

Linear least squares on the given data, i vs. $\omega^{1/2}$, yields the Levich plot

$$i = -0.488\,57 mA.cm^{-2} + \left(0.49771\ mA.s^{1/2}.cm^{-2}\right)\omega^{1/2}$$

From eq. (9.107),

$$
\begin{aligned}
i &= \left(0.62zFC_oD^{2/3}K_v^{-1/6}\right)\sqrt{\omega} \\
Slope &= \left(0.62zFC_oD^{2/3}K_v^{-1/6}\right) \\
D &= \left(\frac{Slope}{0.62zFC_oK_v^{-1/6}}\right)^{3/2} \\
D &= \left[\frac{0.49771x10^{-3}\ A.s^{1/2}.cm^{-2}}{(0.62)\,(2)\left(96,500\ \frac{A.s}{mol}\right)\left(2.21x10^{-6}\frac{mol}{cm^3}\right)(0.056\ cm^2/s)^{-1/6}}\right]^{3/2} \\
D &= 3.97\times10^{-5}cm^2/s
\end{aligned}
$$

9.17 It is desired to produce copper according to the electrolytic cell diagram

$$(-)\,Steel|\,Cu^{+2}/Cu,\ H^{+}/H_2|\,|H_2O/O_2\,|PbO_2\,(+)$$
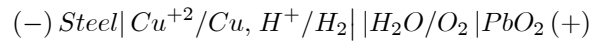
for 24 hours at which time the cathodes are mechanically stripped (removed). Copper is reduced from an aqueous copper sulfate ($Cu\,SO_4$) and sulfuric acid

(H_2SO_4) solution at 35^oC. The anodes operate at 100% current efficiency with respect to oxygen evolution and that for the cathodes is $\epsilon = 90\%$ due to hydrogen evolution. These type of electrodes are connected in parallel within 100 tanks that operate at 2.4 *volts* each and the electrodes have a specific submerged area A_e. Use the following relevant data to perform some calculati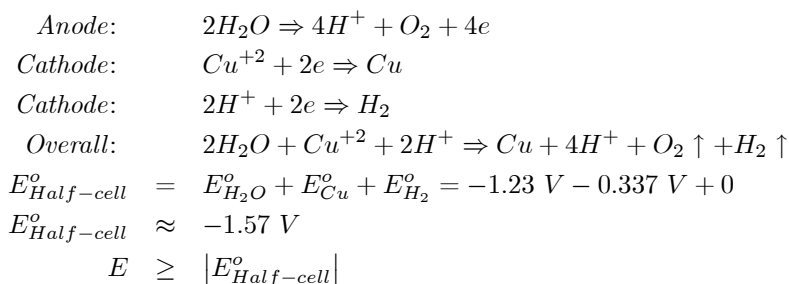ons given below. Cost of electricity per $kW.h$: $C_e = 0.30$ \$/$kW.h$, Market price of copper: $C_{market} = \$0.70/Kg$, and

$$P = 72 \ kW \ \text{(Power)} \qquad A_w = 63.54 \ g/mol$$
$$E = 2.4 \ V \qquad D_{Cu^{+2}} = 1.24x10^{-5} \ cm^2/s$$
$$N_T = 100 \ \text{(Tanks)} \qquad K_v = 0.80 \ cm^2/s$$
$$N_a = 30 \ \text{(Anodes per tank)} \qquad v_x = 0.312 \ cm/s \ \text{(Velocity of } Cu^{+2})$$
$$N_c = 29 \ \text{(Cathodes per tank)} \qquad d = 6 \ cm \ \text{(electrode distance)}$$
$$A_e = 0.80 \ m^2 \ \text{(Electrode area)} \qquad C_e = 0.30 \ \$/kW.h \ \text{(Electricity)}$$

(a) Write down all the reactions and the standard half-cell potential involved in this electrowinning process. What should the applied potential be? Calculate (b) the total current, the anodic and cathodic current densities, and (c) S_c, R_e, S_h and C_b in g/l per tank. Let the anode characteristic length be $L = \sqrt{A_e}$. Use the Sherwood number ($S_h < 100$) and the Reynolds number ($R_e < 2,300$) to assure force laminar flow. Determine (d) the production rate (P_R) and the total weight produced (W_T) in 24 hours, (e) the energy consumption (γ). Use your engineering economics skills to estimate (f) the cost of energy consumed (C_{te}), the total cost of production (C_{prod}) and the gross income (G_I) in 24 *hours* if the industrial cost of electric energy and the market price of copper are $C_e = \$0.30 \ kW.h$ and $C_{market} = \$3.193/lb = \$7.041/Kg$, respectively. [Solutions: (a) $E^o_{Half-cell} \approx -1.57 \ V$, (b) $i_c = 0.001293 \ A/cm^2$, (c) $S_h \approx 39$ and $C_b = 78.80 \ g/l$].

Solution:
(a) *The reactions, the standard half-cell potential and the applied potential are*

$$\begin{aligned} \text{Anode:} \qquad & 2H_2O \Rightarrow 4H^+ + O_2 + 4e \\ \text{Cathode:} \qquad & Cu^{+2} + 2e \Rightarrow Cu \\ \text{Cathode:} \qquad & 2H^+ + 2e \Rightarrow H_2 \\ \text{Overall:} \qquad & 2H_2O + Cu^{+2} + 2H^+ \Rightarrow Cu + 4H^+ + O_2 \uparrow + H_2 \uparrow \\ E^o_{Half-cell} = \ & E^o_{H_2O} + E^o_{Cu} + E^o_{H_2} = -1.23 \ V - 0.337 \ V + 0 \\ E^o_{Half-cell} \approx \ & -1.57 \ V \\ E \geq \ & \left| E^o_{Half-cell} \right| \end{aligned}$$

(b) *The total current*

$$I = \frac{P}{E} = \frac{72 \times 10^3 \text{ A V}}{2.4 \text{ V}} = 3.0 \times 10^4 \text{ A}$$

Electrode areas per tank:

$$A_a = N_T N_a A_e = (100)(30)(8,000 \text{ cm}^2) = 24.0 x 10^6 \text{ cm}^2$$
$$A_c = N_T N_c A_e = (100)(29)(8,000 \text{ cm})^2 = 23.2 x 10^6 \text{ cm}^2$$

Current densities per tank:

$$i_a = \frac{I}{A_a} = \frac{3.0 \times 10^4 \text{ A}}{24.0 x 10^6 \text{ cm}^2} = 0.001250 \ A/cm^2 = 1.250 \ \frac{A}{m^2}$$
$$i_c = \frac{I}{A_c} = \frac{3.0 \times 10^6 \text{ A}}{23.2 x 10^6 \text{ cm}^2} = 0.001293 \ A/cm^2 = 1.293 \ \frac{A}{m^2}$$

(c) *Assume force laminar flow. The Schmidt (S_c), Reynolds (R_e) number and the anode length are*

$$S_c = K_v/D = (0.80 \ cm^2/s)/(1.24 x 10^{-5} \ cm^2/s) = 64.52 x 10^3$$
$$R_e = v_x d/K_v = (0.312 \ cm/s)(6 \ cm)/(0.80 \ cm^2/s) = 2.34$$

From eq. (9.101) along with the anode characteristic length (L), the Sherwood number is

$$L = \sqrt{A_e} = \sqrt{0.8 \ m^2} = 0.8944 \ m^2 = 89.44 \ cm^2$$
$$S_h = \left(\frac{9}{5}\right)\left(\frac{v_x d^2}{LD}\right)^{1/3} = \left(\frac{9}{5}\right)\left[\frac{(0.312 \ cm/s)(6 \ cm)^2}{(89.44 \ cm)(1.24 x 10^{-5} \ cm^2/s)}\right]^{1/3}$$
$$S_h \approx 39$$

or from eq. (9.97)

$$S_h = \left(\frac{9}{5}\right)\left[\frac{d}{L}(S_c R_e)\right]^{1/3}$$
$$S_h = \left(\frac{9}{5}\right)\left[\left(\frac{6}{89.44}\right)(64.52 * 10^3)(2.34)\right]^{1/3} \approx 39$$

Using eq. (9.97) for one tank yields the cathodic current density as the limiting current density ($i_c = i_L$) and the bulk concentration (C_b) in g/l per tank.

$$i_c = \frac{9zFC_b}{5}\left(\frac{v_x d^2 D^2}{L^4}\right)^{1/3}$$

$$C_b = \frac{5i_c}{9zF}\left(\frac{L^4}{v_x d^2 D^2}\right)^{1/3}$$

$$C_b = \frac{(5)\left(0.001293\ A/cm^2\right)}{(9)(2)\left(96,500\ \frac{A.s}{mol}\right)}\left[\frac{(89.44\ cm)^4}{\left(0.312\ \frac{cm}{s}\right)(6\ cm)^2\left(1.24x10^{-5}\ \frac{cm^2}{s}\right)^2}\right]^{1/3}$$

$$C_b = 1.24\times10^{-3}\ mol/cm^3 = 1.24\ \ mol/l$$

$$C_b = (1.24\ \ mol/l)\,(63.55\ g/mol) \simeq 78.80\ g/l$$

Alternatively, using eqs. (9.94) and (7.87b) with $\Delta C = C_b$ *gives per tank*

$$S_h = \left(\frac{2}{3}\right)(S_c)^{1/3}(R_e)^{1/2} = \left(\frac{2}{3}\right)\left(64.52x10^3\right)^{1/3}(2.34)^{1/2} \approx 41$$

$$C_b = \frac{i_c L}{zFDS_h} = \frac{\left(0.001293\ \frac{A}{cm^2}\right)(89.44\ cm)}{(2)\left(96,500\ \frac{A.s}{mol}\right)\left(1.24\times10^{-5}\ \frac{cm^2}{s}\right)(41)}$$

$$C_b = 1.18x10^{-3}\ mol/cm^3 = 1.18\ mol/l$$

$$C_b = (1.18\ mol/l)\,(63.55\ g/mol) = 75\ g/l$$

Both equations give fairly similar results. Let's use the results given by eq. (4.94) in eq. (9.87b).

(d) *Production rate (*P_R*) and total weight produced (*W_T*) in 24 hours:*

$$P_R = \frac{\epsilon i_c A_c A_w}{zF} = \frac{(0.90)\left(0.001293\ \frac{A}{cm^2}\right)\left(23.2x10^6\ cm^2\right)\left(63.55\ \frac{g}{mol}\right)}{(2)(96,500\ A.s/mol)}$$

$$P_R = 8.8897\ g/\sec = 32.003\ Kg/h = 768.07\ Kg/day \quad \text{(Total)}$$

$$W_T = (32.003\ Kg/h)\,(24\ h) = 768.07\ Kg \quad \text{(Total)}$$

$$w_t = W_T/N_T = (768.07\ Kg)\,/100 = 7.68\ Kg \quad \text{(Per tank)}$$

$$w_c = (7.68\ Kg)\,/29 = 0.26483\ Kg = 264.83\ grams \quad \text{(Per cathode)}$$

The energy consumption is

$$\gamma = \frac{P}{P_R} = \frac{72\ kW}{32.003\ Kg/h} = 2.25\ kW.h/Kg \quad \text{(Total)}$$

$$\gamma = 0.0225\ kW.h/Kg \quad \text{(Per tank)}$$

$$\gamma = 7.76x10^{-4}\ kW.h/Kg \quad \text{(Per cathode)}$$

If the cost of electricity per kW.h is $C_e = 0.30$ $/kW.h, then the cost of energy consumed is

$$
\begin{aligned}
C_{te} &= C_e \gamma W_T = (0.30 \ \$/kW.h) \ (2.25 \ kW.h/Kg) \ (768.07 \ Kg) \\
C_{te} &= \$518.45 \quad (Total) \\
C_t &= C_{te}/N_T = (\$518.45) \ /100 = \$5.1845 \quad (Per \ tank) \\
C_c &= C_{te}/ \ (N_c) = (\$518.45) \ /29 = \$17.88 \quad (Per \ Cathode)
\end{aligned}
$$

Thus, the cost of production is

$$
\begin{aligned}
C_{prod} &= \frac{C_{te}}{W_T} = \frac{\$518.45}{768.07 \ Kg} \\
C_{prod} &= \$0.68/Kg
\end{aligned}
$$

If the market price is $C_{market} = \$3.193/lb = \$7.041/Kg$, then the gross income in 24 hours is

$$
\begin{aligned}
G_I &= (C_{market} - C_{prod}) \ (W_T) = (\$7.041/Kg - \$0.68/Kg) \ (768.07 \ Kg) \\
G_I &= \$4,885.70 \quad (For \ a \ 24\text{-}hour \ run)
\end{aligned}
$$

This result is rather low. What can be improved for a higher G_I?

9.18 A Hall-Heroult (HH) cell is used to produce molten aluminum containing hydrogen. The hydrogen content can be removed by allowing a thin film of molten aluminum flow down on an inclined plane during pouring in vacuum. The incline plane is shown below and it is in the L-w-δ space, where δ is the film thickness and w is the width.

HH Cell (Effect of gravity)
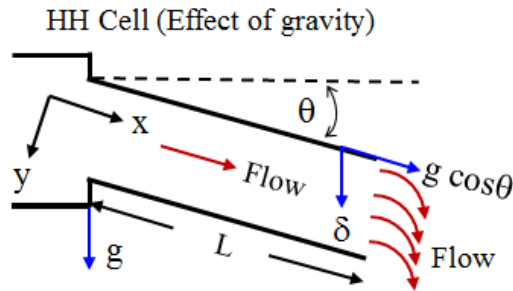
The weight-induced and gravity-induced free fluid flow occurs in the x-direction. Using Newton's law of viscosity yields the force acting on the fluid in the direction of the flow, together with the moment balance. Thus, this phenomenon is described by an ordinary differential equation.

$$\eta_v \frac{d^2 v_x}{dy^2} = -\rho g \cos(\theta) \quad \text{with BC's} \left\{ \begin{array}{ll} v_x = 0 & @ \ y = \delta \\ v_x > 0 & @ \ y > 0 \end{array} \right\}$$

where η_v = Fluid viscosity, v_x = Fluid velocity and ρ = Density of the fluid. Solve this differential equation and calculate the average a) value of the boundary layer, b) velocity $\overline{v_x}$, c) molar flux of hydrogen due to both diffusion and convection effects, d) time it takes to remove the dissolved hydrogen along the channel length L and the amount of hydrogen being removed, and e) the Reynolds number. Given data:

$\rho = \rho_{Al} = 2.5 \ g/cm^3$	$w = 50 \ cm$
$\eta_v = 40 \ g.cm^{-1}s^{-1}$	$L = 100 \ cm$
$D_H = 5x10^{-3} \ cm^2/s$	$\theta = 2^o$
$C_{H,b} = 30 \ mol/cm^3$	$\dot{m} = 100 \ g/s$
$C_H = 0 \quad @ \ y = 0$	$g = 981 \ cm/s^2$

Solution:

The solution of the above differential equation is

$$\frac{dv_x}{dy} = -\frac{\rho g \cos(\theta)}{\eta_v} y$$

$$\int_0^{v_x} dv_x = -\frac{\rho g \cos(\theta)}{\eta_v} \int_\delta^y y dy$$

$$v_x = \frac{\rho g \cos(\theta)}{2\eta_v} \left(\delta^2 - y^2 \right)$$

$$v_{x,\max} = \frac{\rho g \delta^2 \cos(\theta)}{2\eta_v}$$

The average fluid velocity is

$$\overline{v_x} = \frac{1}{\delta} \int_0^\delta v_x dy = \frac{1}{\delta} \int_0^\delta \frac{\rho g \cos(\theta)}{2\eta_v} \left(\delta^2 - y^2 \right) dy$$

$$\overline{v_x} = \frac{1}{\delta} \left[\frac{\rho g \cos(\theta)}{2\eta_v} \right] \left[\delta^2 y - \frac{y^3}{3} \right]_o^\delta$$

$$\overline{v_x} = \frac{\rho g \delta^2 \cos(\theta)}{3\eta_v}$$

$$\overline{v_x} = \frac{2}{3} v_{x,\max}$$

The cross-sectional of the flowing fluid is $A = \delta w$ and the average mass flow rate is

$$\dot{m} = \overline{v_x}\rho A$$

$$\dot{m} = \frac{\rho g \delta^3 w \cos(\theta)}{3\eta_v}$$

a) *Thus, the average boundary layer becomes*

$$\delta = \left[\frac{3\eta_v \dot{m}}{\rho g w \cos(\theta)}\right]^{1/3} = 0.46 \ cm$$

b) *The average fluid velocity is*

$$\overline{v_x} = \frac{\rho g \delta^2 \cos(\theta)}{3\eta_v} = 4.34 \ cm/s$$

c) *The average molar flux mathematical model is defined in Chapter 4. Using eq. (4.9a) along with $d\phi/dx = 0$ gives*

$$J_x = J_d + J_c = -D_H \frac{\partial C}{\partial x} + \overline{v_x} C_{H,b}$$

$$J_x = -D_H \frac{C_s - C_x}{\delta} + \overline{v_x} C_{H,b}$$

Using the boundary conditions $C_s = 0$ at $y = 0$ and $C_x = C_{H,b}$ at $y = \delta$ yields

$$J_x = \frac{D_H C_{H,b}}{\delta} + \overline{v_x} C_{H,b}$$

$$J_x = C_{H,b}\left(\frac{D_H}{\delta} + \overline{v_x}\right) = 130.53 \ \frac{mol}{cm^2 s}$$

d) *The average time along the channel length is*

$$t = \frac{L}{\overline{v_x}} = 23.04 \ sec$$

Then, the amount of hydrogen removed is

$$m = t\dot{m} = 2,304 \ g \approx 2.30 \ Kg$$

e) *Using eq. (9.78) yields the Reynolds number along with $d = \delta$*

$$R_e = \frac{\rho \overline{v_x} \delta}{\eta_v} = 0.13$$

9.19 *An electrowinning cell produces $10 \ Kg/h$ of nickel (Ni) at a current efficiency (ϵ) of 80%. The cell contains 20 cathodes and operates at a current of*

215 A/m^2 and a potential of 2 V. Determine **(a)** the energy consumption, **(b)** the flow rate of the electrolyte and **(c)** the cathode length for a width of 1 m. The concentration of nickel cations is 35 g/l. **(d)** Plot eq. (9.25) and explain the result.

Solution:

$Ni^{2+} + 2e = Ni$ @ $E = 2$ V and $i = 215$ A/m^2 with $z = 2$

$P_R = 10$ $Kg/h = 10^4$ g/h, $N = 20$, $A_{w,Ni} = 58.71$ g/mol

$C_o = 35$ $g/l = 5.96x10^{-4}$ mol/cm^3

(a) From, eq. (9.23),

$$
\begin{aligned}
A_s &= zFP_r/\left(\epsilon i A_w\right) = 53.10 \ m^2 \\
I &= iA_s = 11,416.20 \ A \\
P &= EI = 22.83 \ kW \\
\gamma &= P/P_R = 2.28 \ kW.h/Kg
\end{aligned}
$$

(b) The flow rate of the electrolyte:

$$F_r = P_r/C_o = 4.76 \ l/min$$

(c) The cathode length:

$$
\begin{aligned}
A_c &= A_s/\left(2N\right) = 1.3275 \ m^2 \\
L &= A_c/w = 1.3275 \ m
\end{aligned}
$$

(d) From eq. (9.25), the simplified energy consumption equation becomes

$$\gamma = 1.83/\epsilon \qquad \text{(in } kW.h/Kg)$$

which is plotted in figure given below indicating that the energy consumption is strongly dependent on the current efficiency since γ is inversely proportional to ϵ. However, this strong dependency begins to have a lesser effect when $\epsilon \geq 0.25$ and when $\epsilon > 0.80$ the energy consumption is significantly reduced.

Let $y = \gamma$ and $x = \epsilon$ so that $y = 1.83/x$.
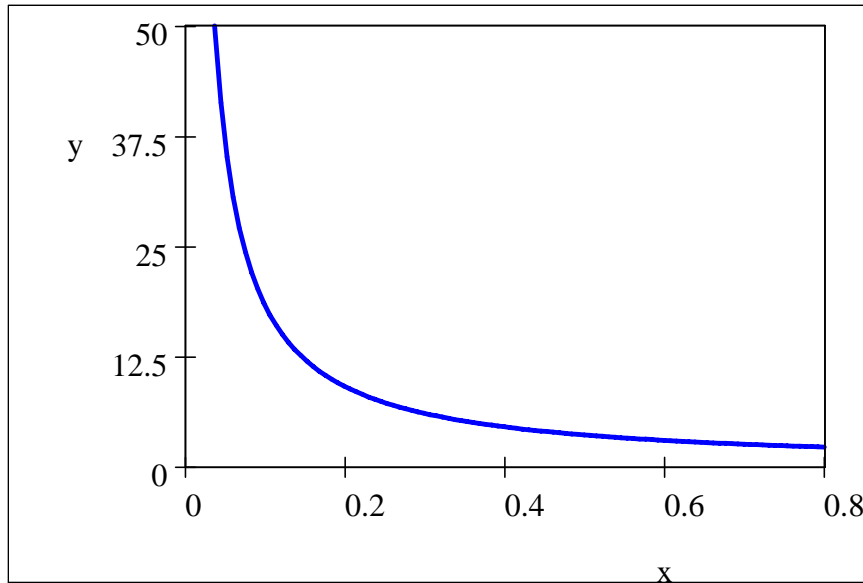
9.20 Below is an electrolytic cell diagram used in an electrowinning factory for producing solid copper on cathode electrodes.

$$(-)\,Steel|\,Cu^{+2}/Cu,\,H^+/H_2|\,|H_2O/O_2\,|PbO_2\,(+)$$
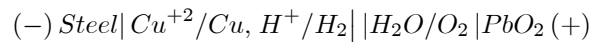
Recall that the cathodes are mechanically stripped (removed) after the electrowinning run is accomplished. The electrolyte used in this electrowinning operation contains aqueous copper sulfate $(Cu\,SO_4)$ and sulfuric acid (H_2SO_4) solution, and it is maintained at 35^oC. Assume that the anodes operate at 100% current efficiency with respect to oxygen evolution and that for the cathodes is $\epsilon = 88\%$ due to hydrogen evolution. These type of electrodes are connected in parallel within 80 tanks that operate at 2.6 *volts* each and the electrodes have a specific submerged area A_e. Use the following relevant data to perform some calculations given below. The average retail price of electricity (cost of electricity) per kWh: $C_e = 0.14\ \$/kW.h$, Market price of copper: $C_{market} = \$0.17/Kg$, and

$P = 72\ kW$ (Power)	$A_w = 63.54\ g/mol$
$E = 2.6\ V$	$D_{Cu^{+2}} = 1.24x10^{-5}\ cm^2/s$
$N_T = 100$ (Tanks)	$K_v = 0.80\ cm^2/s$
$N_a = 30$ (Anodes per tank)	$v_x = 0.312\ cm/s$ (Velocity of Cu^{+2})
$N_c = 29$ (Cathodes per tank)	$d = 6\ cm$ (electrode distance)
$A_e = 0.80\ m^2$ (Electrode area)	$C_e = 0.14\ \$/kW.h$ (Electricity)

(a) Write down all the reactions and the standard half-cell potential involved in this electrowinning process. What should the applied potential be

compared to the half-cell potential? Is the given operating potential (2.6 *volts*) suitable for this electrowinning? Calculate **(b)** the total current, the anodic and cathodic current densities, and **(c)** S_c, R_e, S_h and C_b in g/l per tank. Let the anode characteristic length be $L = \sqrt{A_e}$. Use the Sherwood number ($S_h < 100$) and the Reynolds number ($R_e < 2,300$) to assure force laminar flow. Determine **(d)** the production rate (P_R) and the total weight produced (W_T) in 24 hours, **(e)** the energy consumption (γ). Use your engineering economics skills to estimate **(f)** the cost of energy consumed (C_{te}), the total cost of production (C_{prod}) and the gross income (G_I) in 24 *hours* if the industrial cost of electric energy and the market price of copper are $C_e = \$0.30$ $kW.h$ and $C_{market} = \$3.193/lb = \$7.041/Kg$, respectively. [Solutions: (a) $E^o_{Half-cell} \approx -1.57\ V$, (b) $i_c = 0.001194\ A/cm^2$, (c) $S_h \approx 39$ and $C_b = 73.08$ g/l].

Solution:

(a) *The reactions, the standard half-cell potential and the applied potential are*

$$
\begin{aligned}
Anode{:} \qquad & 2H_2O \Rightarrow 4H^+ + O_2 + 4e \\
Cathode{:} \qquad & Cu^{+2} + 2e \Rightarrow Cu \\
Cathode{:} \qquad & 2H^+ + 2e \Rightarrow H_2 \\
Overall{:} \qquad & 2H_2O + Cu^{+2} + 2H^+ \Rightarrow Cu + 4H^+ + O_2 \uparrow + H_2 \uparrow \\
E^o_{Half-cell} \; = \; & E^o_{H_2O} + E^o_{Cu} + E^o_{H_2} = -1.23\ V - 0.337\ V + 0 \\
E^o_{Half-cell} \; \approx \; & -1.57\ V \\
E \; \geq \; & \left| E^o_{Half-cell} \right|
\end{aligned}
$$
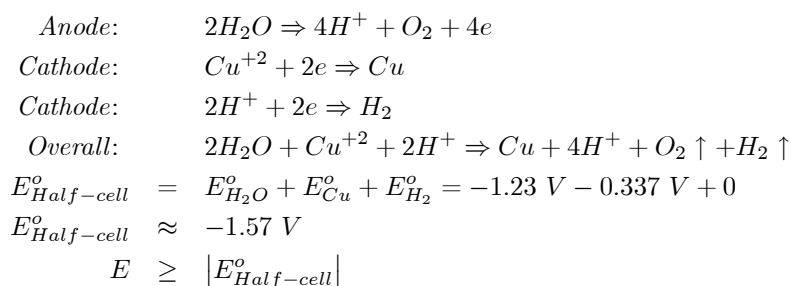
The applied potential should be $E \geq \left| E^o_{Half-cell} \right|$. So the given operating potential (2.6 *volts*) is suitable for this electrowinning cell because 2.6 *volts* $> \left| E^o_{Half-cell} \right|$.

(b) *The total current*

$$
I = \frac{P}{E} = \frac{72 \times 10^3\ \text{A V}}{2.6\ \text{V}} = 27,692\ \text{A}
$$

Electrode areas per tank:

$$
\begin{aligned}
A_a \; = \; & N_T N_a A_e = (100)\,(30)\,\left(8,000\ \text{cm}^2\right) = 24.0 x 10^6\ \text{cm}^2 \\
A_c \; = \; & N_T N_c A_e = (100)\,(29)\,(8,000\ \text{cm})^2 = 23.2 x 10^6\ \text{cm}^2
\end{aligned}
$$

Current densities per tank:

$$i_a = \frac{I}{A_a} = \frac{27,692 \text{ A}}{24.0 x 10^6 \text{ cm}^2} = 0.001154 \ A/cm^2 = 1.250 \ \frac{A}{m^2}$$

$$i_c = \frac{I}{A_c} = \frac{27,692 \text{ A}}{23.2 x 10^6 \text{ cm}^2} = 0.001194 \ A/cm^2 = 1.293 \ \frac{A}{m^2}$$

(c) *Assume force laminar flow. The Schmidt* (S_c)*, Reynolds* (R_e) *number and the anode length* (L) *are*

$$S_c = K_v/D = \left(0.80 \ cm^2/s\right) / \left(1.24 x 10^{-5} \ cm^2/s\right) = 64.52 x 10^3$$

$$R_e = v_x d/K_v = \left(0.312 \ cm/s\right) \left(6 \ cm\right) / \left(0.80 \ cm^2/s\right) = 2.34$$

From eq. (9.101) along with the anode characteristic length (L), the Sherwood number is

$$L = \sqrt{A_e} = \sqrt{0.8 \ m^2} = 0.8944 \ m^2 = 89.44 \ cm^2$$

$$S_h = \left(\frac{9}{5}\right)\left(\frac{v_x d^2}{LD}\right)^{1/3} = \left(\frac{9}{5}\right)\left[\frac{\left(0.312 \ cm/s\right)\left(6 \ cm\right)^2}{\left(89.44 \ cm\right)\left(1.24 x 10^{-5} \ cm^2/s\right)}\right]^{1/3}$$

$$S_h \approx 39$$

or from eq. (9.97)

$$S_h = \left(\frac{9}{5}\right)\left[\frac{d}{L}\left(S_c R_e\right)\right]^{1/3}$$

$$S_h = \left(\frac{9}{5}\right)\left[\left(\frac{6}{89.44}\right)\left(64.52 * 10^3\right)\left(2.34\right)\right]^{1/3} \approx 39$$

Using eq. (9.97) for one tank yields the cathodic current density as the limiting current density $(i_c = i_L)$ *and the bulk concentration* (C_b) *in g/l per tank. Thus,*

$$i_c = \frac{9zFC_b}{5}\left(\frac{v_x d^2 D^2}{L^4}\right)^{1/3}$$

$$C_b = \frac{5i_c}{9zF}\left(\frac{L^4}{v_x d^2 D^2}\right)^{1/3}$$

$$C_b = \frac{(5)\left(0.001194 \ A/cm^2\right)}{(9)(2)\left(96,500 \ \frac{A.s}{mol}\right)}\left[\frac{\left(89.44 \ cm\right)^4}{\left(0.312 \ \frac{cm}{s}\right)\left(6 \ cm\right)^2\left(1.24 x 10^{-5} \ \frac{cm^2}{s}\right)^2}\right]^{1/3}$$

$$C_b = 1.15 \times 10^{-3} \ mol/cm^3 = 1.24 \ mol/l$$

$$C_b = \left(1.15 \ mol/l\right)\left(63.55 \ g/mol\right) = 73.08 \ g/l$$

Alternatively, using eqs. (9.94) and (7.87b) with $\Delta C = C_b$ gives per tank

$$S_h = \left(\frac{2}{3}\right)(S_c)^{1/3}(R_e)^{1/2} = \left(\frac{2}{3}\right)(64.52x10^3)^{1/3}(2.34)^{1/2} \approx 41$$

$$C_b = \frac{i_c L}{zFDS_h} = \frac{\left(0.001194 \ \frac{A}{cm^2}\right)(89.44 \ cm)}{(2)\left(96,500 \ \frac{A.s}{mol}\right)\left(1.24 \times 10^{-5} \ \frac{cm^2}{s}\right)(41)}$$

$$C_b = 1.189x10^{-3} \ mol/cm^3 = 1.19 \ mol/l$$

$$C_b = (1.19 \ mol/l)(63.55 \ g/mol) = 75.63 \ g/l$$

Both equations give fairly similar results. Let's use the results given by eq. (4.94) in eq. (9.87b).

(d) *Production rate (P_R) and total weight produced (W_T) in 24 hours:*

$$P_R = \frac{\epsilon i_c A_c A_w}{zF} = \frac{(0.88)\left(0.001194 \ \frac{A}{cm^2}\right)(23.2x10^6 \ cm^2)\left(63.55 \ \frac{g}{mol}\right)}{(2)(96,500 \ A.s/mol)}$$

$$P_R = 8.0266 \ g/\sec = 28.90 \ Kg/h \simeq 694 \ Kg/day \quad \text{(Total)}$$

$$W_T = (28.90 \ Kg/h)(24 \ h) = 694 \ Kg \quad \text{(Total)}$$

$$w_t = W_T/N_T = (694 \ Kg)/100 = 6.94 \ Kg \quad \text{(Per tank)}$$

$$w_c = (6.94 \ Kg)/29 = 0.23931 \ Kg = 239.31 \ grams \quad \text{(Per cathode)}$$

The energy consumption is

$$\gamma = \frac{P}{P_R} = \frac{72 \ kW}{28.90 \ Kg/h} = 2.49 \ kW.h/Kg \quad \text{(Total)}$$

$$\gamma = (2.49 \ kW.h/Kg)/100 = 0.0249 \ kW.h/Kg \quad \text{(Per tank)}$$

$$\gamma = 8.59x10^{-2} \ kW.h/Kg \quad \text{(Per cathode)}$$

If the cost of electricity per kW.h is $C_e = 0.14 \ \$/kW.h$, then the cost of energy consumed is

$$C_{te} = C_e\gamma W_T = (0.14 \ \$/kW.h)(2.49 \ kW.h/Kg)(694 \ Kg)$$

$$C_{te} = \$241.93 \quad \text{(Total)}$$

$$C_t = C_{te}/N_T = (\$241.93)/100 = \$2.4193 \quad \text{(Per tank)}$$

$$C_c = C_{te}/(N_c) = (\$518.45)/29 = \$8.34 \quad \text{(Per Cathode)}$$

Thus, the cost of production is

$$C_{prod} = \frac{C_{te}}{W_T} = \frac{\$241.93}{694 \ Kg}$$

$$C_{prod} = \$0.35/Kg$$

If the market price is $C_{market} = \$3.193/lb = \$7.041/Kg$, then the gross income in 24 hours is

$$G_I = (C_{market} - C_{prod})(W_T) = (\$7.041/Kg - \$0.35/Kg)(694\ Kg)$$
$$G_I = \$4,643.60 \quad \text{(For a 24-hour run)}$$

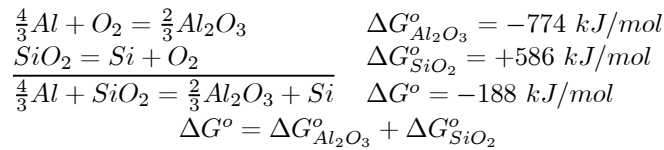This result is rather low. What can be improved for a higher G_I?

Chapter 10

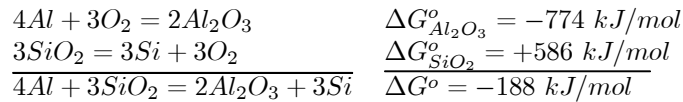# HIGH-TEMPERATURE CORROSION

10.1 A silicon oxide crucible is used to melt pure aluminum in the presence of oxygen at $1300^o C$. a) Will the silicon oxide (SiO_2) corrode? b) What's the oxygen pressure? [Hint: Use Figure 10.1].

Solution:
From Figure 10.1 @ $1300^o C$,

$$\frac{4}{3}Al + O_2 = \frac{2}{3}Al_2O_3 \qquad \Delta G^o_{Al_2O_3} = -774 \; kJ/mol$$
$$\underline{SiO_2 = Si + O_2 \qquad\qquad\qquad \Delta G^o_{SiO_2} = +586 \; kJ/mol}$$
$$\frac{4}{3}Al + SiO_2 = \frac{2}{3}Al_2O_3 + Si \quad \Delta G^o = -188 \; kJ/mol$$
$$\Delta G^o = \Delta G^o_{Al_2O_3} + \Delta G^o_{SiO_2}$$

or

$$4Al + 3O_2 = 2Al_2O_3 \qquad\qquad \Delta G^o_{Al_2O_3} = -774 \; kJ/mol$$
$$\underline{3SiO_2 = 3Si + 3O_2 \qquad\qquad \Delta G^o_{SiO_2} = +586 \; kJ/mol}$$
$$4Al + 3SiO_2 = 2Al_2O_3 + 3Si \quad \Delta G^o = -188 \; kJ/mol$$

The SiO_2 crucible will corrode at $1300^o C$ since molten aluminum is reduced Al_2O_3 (alumina) because $\Delta G^o < 0$.

b) *From eq. (10.5b) and $P_o = 1 \; atm$ (standard pressure),*

$$\Delta G^o = -RT \ln [K]$$
$$\Delta G^o = -RT \ln \frac{[Al_2O_3]^{2/3}}{[Al]^{4/3} [Si] [O_2]} = -RT \ln \left(\frac{1}{[O_2]} \right)$$
$$\Delta G^o = RT \ln [O_2] = RT \ln \left[\frac{P_{O_2}}{P_o} \right]$$

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Thus,

$$P_{O_2} = P_o \exp\left(\frac{\Delta G^o}{RT}\right) = (1 \ atm) \exp\left[\frac{-188x10^3 \ J/mol}{(8.314 \ J/mol.^oK)(1573^oK)}\right]$$
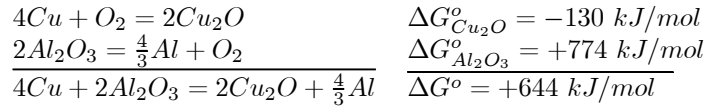
$$P_{O_2} = 5.71x10^{-7} \ atm$$

10.2 An Alumina (Al_2O_3) crucible contains molten copper and oxygen (O_2) at 1300^oC. Determine a) if the crucible will corrode, if so, calculate the oxygen pressure.

Solution:
From Figure 10.1 @ 1300^oC,

$$4Cu + O_2 = 2Cu_2O \quad \Delta G^o_{Cu_2O} = -130 \ kJ/mol$$
$$2Al_2O_3 = \tfrac{4}{3}Al + O_2 \quad \Delta G^o_{Al_2O_3} = +774 \ kJ/mol$$

or

$$4Cu + O_2 = 2Cu_2O \qquad\qquad \Delta G^o_{Cu_2O} = -130 \ kJ/mol$$
$$\underline{2Al_2O_3 = \tfrac{4}{3}Al + O_2} \qquad\qquad \underline{\Delta G^o_{Al_2O_3} = +774 \ kJ/mol}$$
$$4Cu + 2Al_2O_3 = 2Cu_2O + \tfrac{4}{3}Al \quad \Delta G^o = +644 \ kJ/mol$$

The Al_2O_3 crucible will not corrode at 1300^oC because $\Delta G^o > 0$. Therefore, there is no need to calculate the oxygen pressure.

10.3 In the case of thick oxide formation at high temperature, the Pilling-Bedworth theory may have a limited applicability. Explain why this may be the case.

Solution: *Basically, the Pilling-Bedworth theory fails when strains develop during the formation and growth of the oxide scale. Consequently, the scale may rupture or become nonprotective.*

10.4 If the protective nature of an oxide film at room temperature is lost at relatively high temperatures, explain the sequence of the oxide thickening process.

Explanation: *This is the case of oxide film growth in which the mechanical properties and the thermal coefficient of expansion are different from the base metal. Therefore, the scale cracks and spalls. If the nature of the thick oxide is volatile, such as tungsten oxide (WO_3) at $T > 550^oC$, the oxide vaporizes at high pressure.*

10.5 Determine the values of K_w from Figure 10.10 and plot K_w vs. T. What can you conclude from this plot?
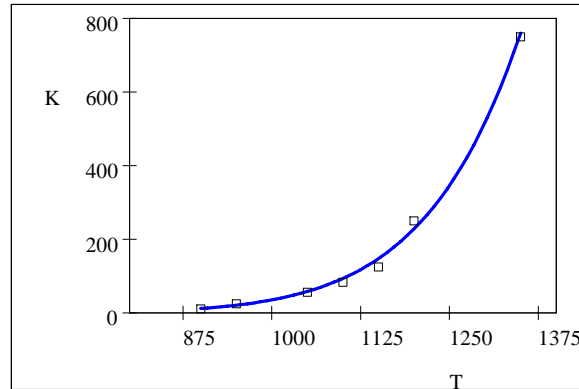
Solution:
From Figure 10.10,

$T\ (^{o}C)$	$K_w\ \left(mg.cm^{-4}h^{-1}\right)$
900	10.40
950	25.00
1050	56.00
1100	83.00
1150	125.0
1200	250.0
1350	750.0

According to these data, the trend is described by the curve fitting equation $\left(R^2 = 0.99\right)$

$$K_w = \left(7 \times 10^{-30}\ mg.cm^{-4}h^{-1}\right) T^{10.234}$$

10.6 Use the data given below to plot K_p vs. $A_{w,oxide}$ (oxide molecular weight) at $T = 1000^{o}C$ and $P_{O_2} = 1\ atm$. What can you conclude from the plot?

Element	Atomic Weight (g/mol)	Molecular Weight (g/mol)	K_p $\left[\left(g^2O_2\right)/cm^4.s\right]$
Co	58.93	$CoO \rightarrow 74.93$	$2.10x10^{-10}$
Cu	63.54	$Cu_2O \rightarrow 143$	$6.30x10^{-9}$
Fe	55.85	$FeO \rightarrow 71.85$	$4.80x10^{-10}$
Si	28.10	$Si\,O_2 \rightarrow 60.10$	$1.20x10^{-12}$

Solution:
Polynomial fit with $R^2 = 0.98$

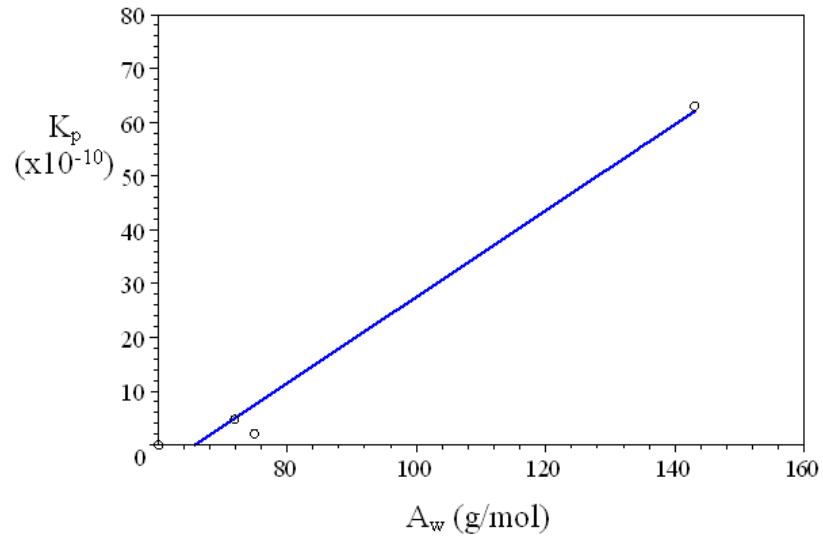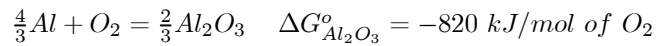$$K_p \left(x10^{-10}\right) = -52.69\,6 + \left(0.8.022\,7\ \frac{mol}{g}\right) A_{w,oxide}$$

Figure 10.1:

One can conclude that K_p increases linearly with molecular weight of the oxide, but more data is needed to be certain of this linear relationship.

10.7 Calculate a) the equilibrium constant K and b) the dissociation oxygen pressure P_{O_2} for the oxidation of aluminum at $1100^O C$.

Solution:

a) *From Figure* 10.1 *@* $1100^o C$,

$$\tfrac{4}{3} Al + O_2 = \tfrac{2}{3} Al_2 O_3 \quad \Delta G^o_{Al_2O_3} = -820 \ kJ/mol \ of \ O_2$$

$$
\begin{aligned}
\Delta G^o &= -RT \ln [K] \\
K &= \exp\left(-\frac{\Delta G^o}{RT}\right) = \exp\left(\frac{820x10^3 \ J/mol}{(8.314 \ J/mol.^oK)(1373^oK)}\right) \\
K &= 1.58x10^{31}
\end{aligned}
$$

b) *Dissociation oxygen pressure and* $P_o = 1 \ atm$ *(standard pressure):*

$$
\begin{aligned}
K &= \frac{[Al_2O_3]^{2/3}}{[Al]^{4/3}[O_2]} = \frac{P_o}{P_{O_2}} \\
P_{O_2} &= \frac{P_o}{K} = \frac{1 \ atm}{1.58x10^{31}} = 6.35x10^{-32} \ atm
\end{aligned}
$$

10.8 If 100 grams of pure aluminum (Al) oxidizes according to the reaction $4Al + 3O_2 = 2Al_2O_3$, calculate the PB ratio defined by

$$PB = V_{Al_2O_3}/V_{Al}$$

where $V's$ are volumes. Data: $\rho_{Al} = 2.70 \ g/cm^3$ and $\rho_{Al_2O_3} = 2.70 \ g/cm^3$.

Solution:

$$
\begin{aligned}
A_{w,Al} &= 26.98 \ g/mol & \rho_{Al} &= 2.70 \ g/cm^3 \\
A_{w,Al_2O_3} &= 101.96 \ g/mol & \rho_{Al_2O_3} &= 3.80 \ g/cm^3
\end{aligned}
$$

If $W_{Al} = 100 \ g$, *then*

$$
\begin{aligned}
W_{Al_2O_3} &= W_{Al}\left[\frac{2A_{w,Al_2O_3}}{4A_{w,Al}}\right] \\
W_{Al_2O_3} &= (100 \ g)\left[\frac{(2)(101.96 \ g/mol)}{(4)(26.98 \ g/mol)}\right] \\
W_{Al_2O_3} &= 188.95 \ g
\end{aligned}
$$

Thus,

$$
\begin{aligned}
V_{Al} &= \frac{W_{Al}}{\rho_{Al}} = \frac{100 \ g}{2.70 \ g/cm^3} = 37.04 \ cm^3 \\
V_{Al_2O_3} &= \frac{W_{Al_2O_3}}{\rho_{Al_2O_3}} = \frac{188.95g}{3.80 \ g/cm^3} = 49.72 \ cm^3
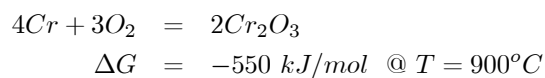\end{aligned}
$$

and

$$
\begin{aligned}
PB &= \frac{V_{Al_2O_3}}{V_{Al}} = \frac{49.72 \ cm^3}{37.04 \ cm^3} \\
PB &= 1.34
\end{aligned}
$$

10.9 A chromium bar is exposed to oxygen gas at 900^oC. Calculate a) the oxygen partial pressure and b) the oxygen activity.

Solution:

a) *Using Figure 10.1 yields*

$$
\begin{aligned}
4Cr + 3O_2 &= 2Cr_2O_3 \\
\Delta G &= -550 \ kJ/mol \ \ @ \ T = 900^oC
\end{aligned}
$$

and

$$\begin{aligned} \Delta G &= -RT \ln(K) \\ K &= \exp\left(-\frac{\Delta G}{RT}\right) = \exp\left[\frac{550x10^3 \ J/mol}{(8.314 \ J/mol.^oK)(1173^oK)}\right] \\ K &= 3.11x10^{24} \end{aligned}$$

The equilibrium constant with the standard pressure $P_o = 1 \ atm = 101 \ kPa$ *is*

$$\begin{aligned} K &= \frac{a^2(Cr_2O_3)}{a^4(Cr)\,a^3(O_2)} = \frac{1}{a^3(O_2)} = \left[\frac{1}{P_{O_2}/P_o}\right]^3 \\ P_{O_2} &= P_oK^{-1/3} = (1atm)\left(3.11x10^{24}\right) \\ P_{O_2} &= 6.85x10^{-9} \ atm = 6.92x10^{-7} \ kPa \end{aligned}$$

b) The activity of oxygen is

$$\begin{aligned} a_{O_2} &= K^{-1/3} = \left(3.11x10^{24}\right)^{-1/3} \\ a_{O_2} &= 6.85x10^{-9} \ mol/l = 6.85x10^{-12} \ mol/cm^3 \end{aligned}$$