1. A sheet of iron (10 cm x 10 cm x 1 mm) is submerged in the Pacific Ocean 12 cm below the surface of the water. An identical sheet of iron is electrically connected to a sheet of platinum, which is identical in size and shape to the sheet of iron and both are submerged in the Pacific Ocean 12 cm below the water's surface. (The platinum and iron are electrically connected by means of a metal wire that exhibits perfect electron conductivity; the metal wire is coated with a non-electrically conducting polymer that prevents water from contacting the wire.)

   (a) Compare the Thermodynamic Driving Forces (TDF) for oxidation of the two sheets of iron (i.e., are the TDFs the same or different?). Briefly explain your answer.

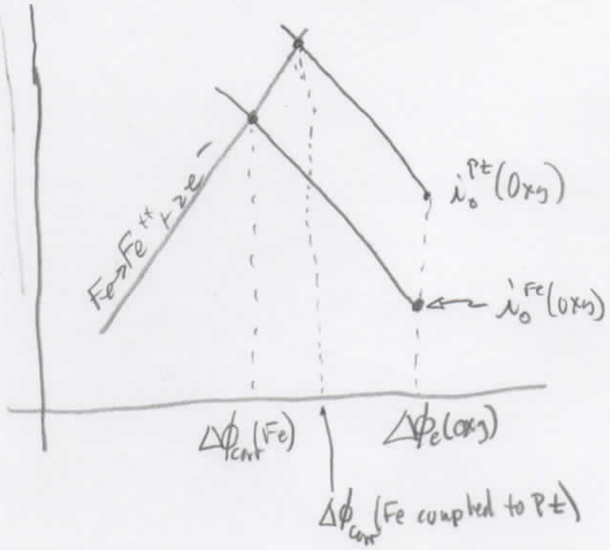
(8)

The TDF is defined as the difference between the equilibrium potential of the electrolyte's redox system and the equilibrium potential of the metal. The equilibrium potentials of both samples of iron are unknown (since the concentration of Fe^{++} in the water adjacent to iron is unknown) but are the same value, the equilibrium potential of the redox system is the same for both pieces of iron. Hence the TDF is the same for both sheets of iron.

(b) Is it likely that the two sheets of iron will exhibit the same or different corrosion rates? Briefly explain your answer.

Pt is a good catalyst for the electrochemical reduction of (i) oxygen. Hence, if transport of O_2 is not the rate limiting step in the reduction of O_2, then:

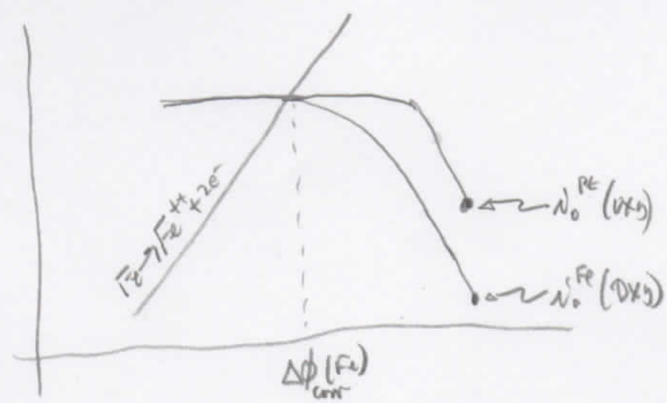
(6)



$\Rightarrow i_{corr}$ (Fe coupled to Pt) $> i_{corr}$ (Fe)

(ii) If transport of O_2 is the RDS then

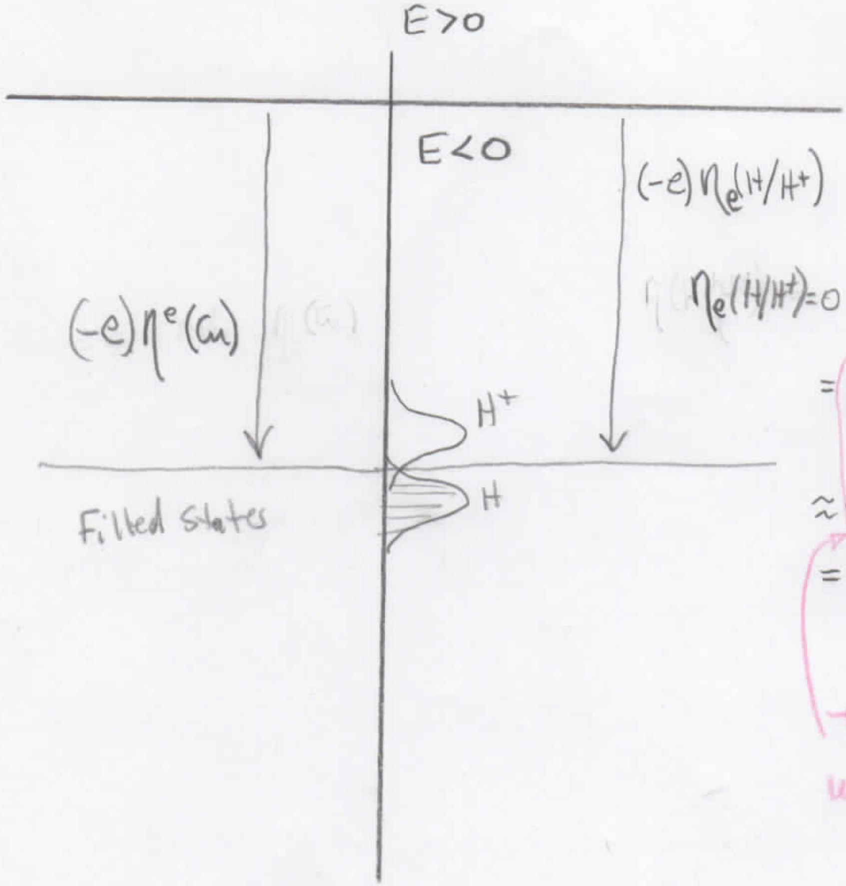
(6.)



In this case i_{corr}^{Fe} is the same for both sheets of Fe

2. (a) Using the Free-Electron Model of metals sketch in the following figure (i) the electrochemical potential at steady-state of conduction band electrons of copper ($= \eta_e^{Cu}$) immersed in oxygen-free water of pH 7, and (ii) the band structure of the H^+/H red-ox system. Specify the numerical value of η_e^{Cu}.

(5)



$$\eta_e(H/H^+) = 0 - \frac{.0592}{2}\log\frac{P_{H_2}}{(10^{-7})^2} = -0.4144\,V_{SHE}$$

($P_{H_2} \to 1$)

$$= \eta_{SHE\ wrt\ Absolute\ Zero\ of\ Energy} - 0.4144\,V_{SHE}$$

$$\approx -4.5\,V - 0.4144\,V$$

$$= -4.9144\,V \text{ wrt Absolute Zero of Energy}$$

This value is not known with great accuracy.

$$\eta_e^{Cu} = 0.337\,V - \frac{.0592}{2}\log\frac{(Cu)}{(Cu^{++})}$$

$$-0.4144 = 0.337 + \frac{.0592}{2}\log(Cu^{++})$$

$$\therefore \log(Cu^{++}) = -25.3851$$

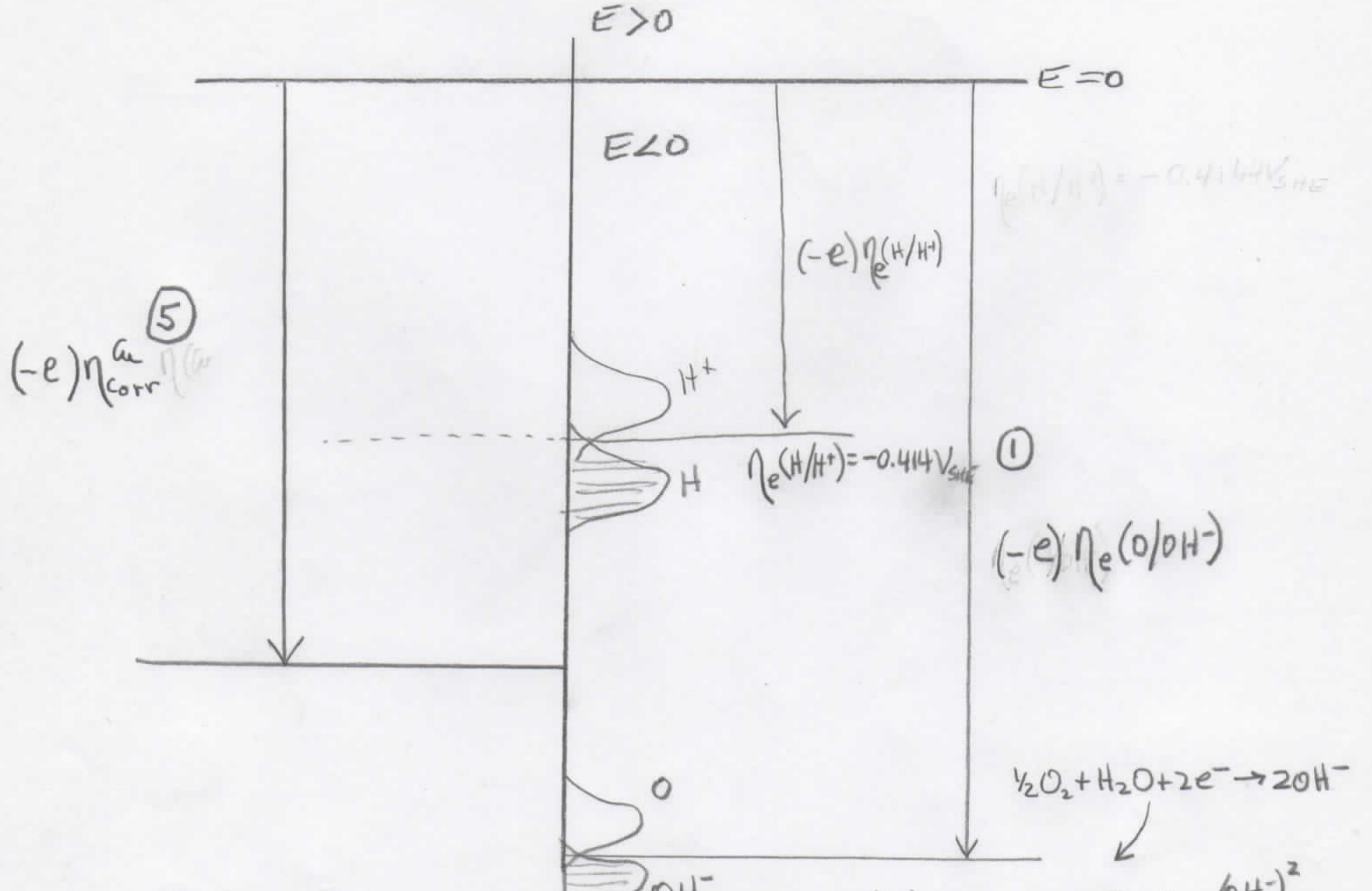
$$\Rightarrow (Cu^{++}) = 4.1 \times 10^{-26}\ M/l$$

$\Rightarrow$ Cu immersed in O_2 free water (pH 7) acts like Pt and Au and other noble metals. That is, the corrosion potential of Cu is $= \eta_e(H/H^+)$

i.e, $\eta_{corr}^{Cu} = \eta_e^{Cu} = \eta_e(H^+/H) = -0.4144\,V_{SHE}$ (5)

$= -4.9144\,V_{Abs\ Zero}$

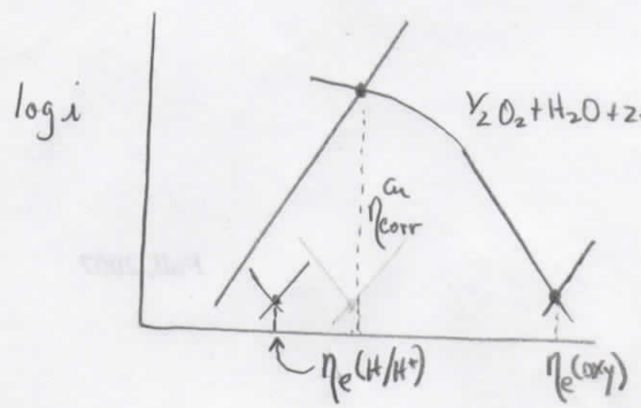
(b) In the following figure sketch the band structure of the H/H^+ and O/OH^- red-ox couples for air-saturated water. On the same figure indicate the approximate location of the electrochemical potential of conduction band electrons in copper that is immersed in air-saturated water. Specify the numerical values of $\eta(H/H^+)$ and $\eta(O/OH^-)$.



$$\eta_e(O/OH^-) = 0.401 - \frac{.0592}{2}\log\frac{(OH^-)^2}{P_{O_2}^{1/2}}$$

$$= 0.401 - \frac{.0592}{2}\log\frac{(10^{-7})^2}{(0.2)^{1/2}}$$

(4) $\therefore \eta_e(O/OH^-) = 0.805 V_{SHE}$



3. The rate of oxidation of bare iron (i.e., no solid corrosion product film) in aqueous solutions of sulfuric acid (H2SO4) for pH between 0 and 4 is described by

$$i_{ox} = 10^{19} \{A/(cm^2 \bullet moles^2/liter^2)\} \bullet [OH^-]^2 \exp(b_{ox}\Delta\phi),$$ where $\Delta\phi$ = potential wrt SHE

In an **air-saturated** solution of sulfuric acid of unknown pH (but in the range of 0 to 4) the corrosion rate and corrosion potential of iron are 1 mA/cm^2 and 0.0 V_{SHE}. When the solution is **saturated with nitrogen gas** the corrosion potential and corrosion rate of iron are 1×10^{-6} A/cm^2 and -0.300 V_{SHE}, and the slope ($\partial \ln_e i_{red}/\partial\Delta\phi$) of the reduction reaction is -23.03 V^{-1}.

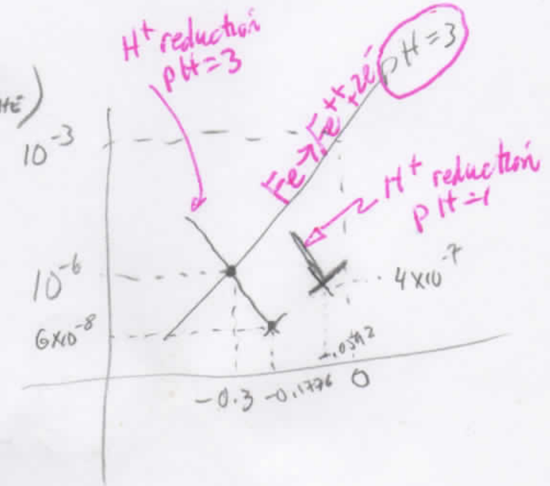
(a) Determine the pH of the solution.

(5)

$$10^{-3} = 10^{19}[OH^-]^2 \exp(b_{ox} \cdot 0 V_{SHE})$$

$$\Rightarrow [OH^-] = 10^{-11} M/l$$

$$\Rightarrow pH = 3$$



(b) What are the corrosion potential and corrosion rate of iron in nitrogen gas-saturated H_2SO_4 if pH =1? $\Rightarrow$ Need $\ln i_{red}$ vs $\Delta\phi$ for pH=1, H_2SO_4.

(i) Calculate $i_o(H)$ for pH=3

$$\ln \frac{i_{red}}{i_{corr}} = (-23.03 V^{-1})(\Delta\phi - \Delta\phi_{corr})$$

$$\ln \frac{i_o}{10^{-6}} = (-23.03 V^{-1})(\Delta\phi_e - (-0.3V))$$

(5) (ii) calculate $\Delta\phi_e$ for pH=3 :

$$= 0 - \frac{.0592}{2} \log \frac{P_{H_2}}{(10^{-3})^2}, \quad P_{H_2} = 1$$

$$= -0.1776 V$$

$$\therefore \ln i_o + \underbrace{\ln \frac{1}{10^{-6}}}_{13.8155} = -23.02(0.1224) = -2.8176$$

7

(10) $\Rightarrow \ln i_o = -16.6331 \Rightarrow i_o = 5.98\times10^{-8}$

$$\ln(4.11\times10^{-7}) - 23.03\,\Delta\phi_{corr} - 1.3634 = \ln 10^{-7} + 23.03\,\Delta\phi_{corr}$$

$$-14.7047 - 23.03\,\Delta\phi_{corr} - 1.3634 = -16.1181 + 23.03\,\Delta\phi_{corr}$$

$$0.05 = 46.06\,\Delta\phi_{corr}$$

(10) $$\Delta\phi_{corr} = 0.0011\ V_{SHE}$$

(vii) Next, determine i_{corr}

$$i_{corr} = i_{ox}(\Delta\phi = 0.0011) = 10^{19}[10^{-13}]^2 \exp(b_{ox}\ 0.0011\ V_{SHE})$$

$\therefore$ need to calculate value of b_{ox}

(10) (vii) $$b_{ox} = \frac{\ln 10^{-3} - \ln 10^{-6}}{0V - (-0.300V)} = \frac{6.9078}{0.3V} = 23.03\ V^{-1}$$

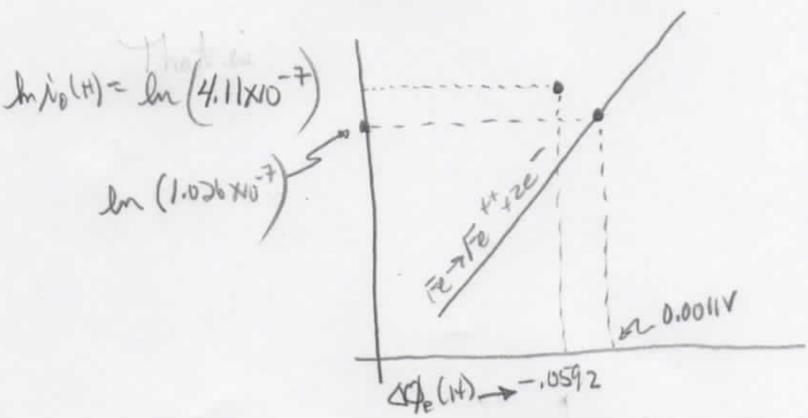
$$\therefore i_{corr} = 10^{19}[10^{-13}]^2 \exp[(23.03V^{-1})(0.0011V)]$$

(viii) (5) $$i_{corr} = 1.026\times10^{-7}\ A/cm^2$$

10pt. **BONUS:**

Note: $(i_{corr}, \Delta\phi_{corr}) = (1.026\times10^{-7}, 0.0011V)$ is very close to

$$(i_o(H), \Delta\phi_e(H)) = (4.11\times10^{-7}, -0.0592V)$$



That is, the rate of oxidation of H is greater than the rate of oxidation of Fe, but we ignored the oxidation of H in the above calculation of i_{corr}. Hence, we need to recalculate i_{corr}, taking into account $i_{ox}(H)$.

That is, we need to calculate $\Delta\phi_{corr}$ at which

$$i_{ox}(Fe) + i_{ox}(H) = i_{red}(H^+)$$

$$i_0 = D P_{H_2}^{\frac{1-\beta}{2}} [H^+]^\beta$$

$$\therefore 5.98\times10^{-8} = D(1)[10^{-3}]^\beta$$

(iii) calculate value of β

$$-23.03\,V^{-1} = -\frac{zF(1-\beta)}{RT}$$ (z = 1)

$$= \frac{-96{,}500(1-\beta)}{1.9872\cdot298\cdot\frac{1}{0.239}}$$

$$= (39.6110)(1-\beta)$$

$$0.5814 = 1-\beta$$

(5) $\Rightarrow \beta = +0.4186$

(iv) calculate i_0 for pH=1:

$\therefore$, for pH=3: $\rightarrow$ $\dfrac{5.98\times10^{-8}}{i_0} = \dfrac{D[10^{-3}]^{0.4186}}{D[10^{-1}]^{0.4186}}$

for pH=1: $\rightarrow$ i_0

$$i_0 = (5.98\times10^{-8})\underbrace{\left(\frac{10^{-1}}{10^{-3}}\right)^{0.4186}}_{6.8737}$$

(5) $\therefore i_0 = 4.11\times10^{-7}$

For pH=1:

(5) (v) calculate $\Delta\phi_e(H)$: $\Delta\phi_e(H) = 0 - \frac{.0592}{2}\log\frac{P_{H_2}}{[10^{-1}]^2} = -.0592V$ (P_{H_2} = 1)

(a) $\ln i_{red}$ vs $\Delta\phi$ for pH=1 is:

$$\therefore \ln\frac{i_{red}}{4.11\times10^{-7}} = -23.03(\Delta\phi + 0.0592V)$$

$$\therefore \ln i_{corr} = \ln(4.11\times10^{-7}) - 23.03(\Delta\phi_{corr} + 0.0592)$$

(b) $\ln i_{ox}$ vs $\Delta\phi$ for pH=1 is:

$$\ln i_{ox} = 10^{19}[10^{-13}]^2 \exp(23.03\,\Delta\phi)$$

$$\therefore \ln i_{ox} = \ln 10^{-7} + 23.03\,\Delta\phi_{corr}$$

(vi) equate $\ln i_{corr}$ from expression of $\ln i_{red}$ to $\ln i_{corr}$ from expression of $\ln i_{ox}$ and solve for $\Delta\phi_{corr}$:

$$\ln(4.11\times10^{-7}) - 23.03\,\Delta\phi_{corr} - 1.3634 = \ln 10^{-7} + 23.03\,\Delta\phi_{corr}$$

Summary of Grading of Problem #3

(a) pH = 3 (5)

(b.) (i) $i_o(H)$ for pH = 3 = 5.98×10^{-8} (10)

(ii) $\Delta\phi_e$(pH = 3) = −0.1776 V (5)

(iii) β_{red} = 0.4186 (5)

(iv) $i_o(H)$ for pH = 1 = 4.11×10^{-7} (5)

(v) $\Delta\phi_e(H)$ pH = 1 = −0.0592 V (5)

(a) $\ln i_{corr}$ vs $\Delta\phi_{corr}$ from H rxn

(b) $\ln i_{corr}$ vs $\Delta\phi_{corr}$ from Fe oxid.

(vi) $\Delta\phi_{corr}$ = 0.0011 V_{SHE} (10)

(vii) b_{ox} = 23.03 V^{-1} (10)

(viii) i_{corr} = 1.026×10^{-7} (5)