MSE 112
Mid-Term EXAM, SPRING 2007

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The use of books or notes during the Exam is NOT permitted.

ALL WORK IS TO BE DONE IN THIS BOOKLET. YOU MAY USE THE BACKS OF PAGES (and page 10, which is blank)

All voltages are measured with respect to SHE.

Logs are in base 10.

1 Joule = 1 volt•coulomb = 0.239 calorie
R=gas constant = 1.9872 cal/(mole°K)
F= Faraday's Constant ≈ 96,500 coulombs/equivalent

Problem	*Point Value*
1	15
2	35
3	24
4	26

$X + ne^- \rightarrow Y$

$$\Delta\phi_e = \Delta\phi_e^\circ - \frac{RT}{nF} \ln \frac{[Y]}{[X]} = (\text{at } 25^\circ C)\ \Delta\phi_e^\circ - (0.059/n\ V) \log_{10} \frac{[Y]}{[X]}$$

$pH = -\log_{10} [H^+]$

$H^+ + OH^- \rightarrow H_2O$ K_W at 25°C = 10^{-14}

$1/2\ O_2 + H_2O + 2e^- \rightarrow 2(OH^-)$ $\Delta\phi_e^\circ = 0.401V$ vs SHE

$Pt^{++} + 2e^- \rightarrow Pt$ $\Delta\phi_e^\circ = 1.118V$ vs SHE

$2H^+ + 2e^- \rightarrow H_2$ $\Delta\phi_e^\circ = 0.0V$ vs SHE

$H_2O + e^- \rightarrow 1/2\ H_2 + (OH^-)$ $\Delta\phi_e^\circ = -0.828V$ vs SHE

$Fe^{++} + 2e^- \rightarrow Fe$ $\Delta\phi_e^\circ = -0.447V$ vs SHE

$Zn^{++} + 2e^- \rightarrow Zn$ $\Delta\phi_e^\circ = -0.760V$ vs SHE

$i_{ox} = (zF/N_o)N_M{'}N_B d_{MB}{}^2(8\pi kT/m)^{1/2}\exp(-\Delta G^{\ddagger}/RT)\exp(zF\beta\,{}^M\Delta^S\phi/RT).$

$i_{red} = zF(C_M - z)N_B d_{MB}{}^2(8\pi kT/m)^{1/2}\exp\{-(\Delta G^{\ddagger} + \Delta G^\circ)/RT\}\exp\{-zF(1-\beta)\,{}^M\Delta^S\phi/RT\}$

$i_o = \{zFd^2(8\pi RT/m)^{1/2}\exp(-[\Delta G^{\ddagger} + \Delta G^{\ddagger}]/RT)\exp(z[1-\beta]F\,\Delta\phi_e{}^\circ/RT)\}[H-](P_{H2}]^{1/2}/[H^+])^{1-\beta}$

$i_o = D[H+](P_{H2}]^{1/2}/[H^+])^{1-\beta}$

$i_o = D(R_aR_bR_c\ldots)\{(P_iP_jP_k\ldots)/(R_aR_bR_c\ldots)\}^{\beta} = D\,(P_iP_jP_k\ldots)(R_aR_bR_c\ldots)^{1-\beta}$

$i_o = D[H^+](P_{H2}]^{1/2}/[H^+])^{1-\beta} = D\,P_{H2}{}^{(1-\beta)/2}\,[H-]^{\beta}$

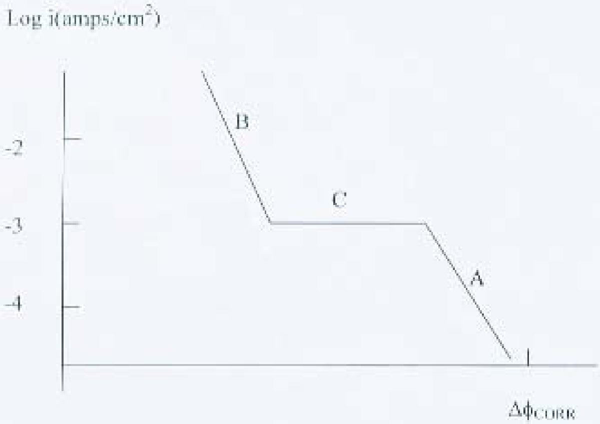
1. (a) Platinum immersed in an air-saturated aqueous electrolyte (e.g., sea water) is referred to as an "oxygen electrode." Platinum immersed in nitrogen-saturated sea water is referred to as a "hydrogen electrode." Explain why these two designations of platinum are appropriate.

Pt noble (state or calculate) + 3

$\Delta\phi_{Pt,air} = \Delta\phi_{O_2}$ (Reducing species) + 3

Oxygen dominates hydrogen + 3

(b) The following is a sketch of the cathodic polarization curve of platinum immersed in air-saturated sea water.



(i) Identify the reduction reactions taking place along A and B.

(A) Reduction of oxygen: $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2(OH^-)$ +2

(B) Reduction of hydrogen: $2H^+ + 2e^- \rightarrow H_2$ +2

(ii) Explain the reason(s) for the zero slope of the curve at C.

The zero slope is the result of the reduction rate of oxygen being limited by the diffusion of oxygen to the surface as opposed to being limited by the charge transfer.

+2

2. Working as a materials engineer at a plant that manufactures thermal insulation, you were asked to select the materials for a tank (10,000 liter volume) that would store the aqueous solution that was left over from the manufacturing process. In the reaction vessel in which the insulation is made, the left-over solution is very acidic and has a pH of 2. The left-over solution is neutralized (i.e., its pH is raised to 7) before it is sent to the 10,000-liter storage vessel.

    For the storage vessel, you selected galvanized carbon-steel (i.e., the inside surface of the tank is coated with an 0.003 inch thick layer of zinc; the steel is 0.25 inch thick and constitutes the majority of the vessel.). You based your selection of galvanized steel on the results of polarization tests that you conducted on zinc immersed in air-free, neutralized (i.e., pH = 7), left-over solution. The solution inside the storage tank is air-free. According to your measurements, the corrosion potential and corrosion rate of zinc are –0.500 V vs. SHE and 5×10^{-7} amps/cm^2, respectively. The slopes of the anodic and cathodic polarization curves are 12.5 V^{-1} and –5.5 V^{-1}, respectively (i.e., for the oxidation reaction, $\log[i/i_o]/[{}^{m}\Delta^{s}\phi - {}^{m}\Delta^{s}\phi_e] = 12.5\ V^{-1}$).

    Based on your measurements of the polarization curves of zinc, you predicted that the zinc coating would survive for approximately 10 years, and that the tank would, therefore, remain leak-free for over 10 years.

    After the storage tank was in service for 1 year, a number of leaks occurred. Inspection of the interior of the tank found that the zinc coating had corroded away, and that the leaks were caused by corrosion of the unprotected steel. Your boss has recommended to the plant manager that you be fired for selecting materials with insufficient corrosion resistance.

    You decide to fight to save your job and request a meeting with your boss and the plant manager. The basis of your defense is the daily measurements of pH of the liquid inside the storage tank. You find that from the time the storage tank was first placed in service, the pH of the spent liquid was not adequately neutralized. Instead of the pH being raised to 7, the pH was consistently raised to only 5.65. Interestingly, you learn that the engineer, who was responsible for insuring that the pH of the solution inside the storage tank was 7, is your boss's son-in-law.

    At the meeting, your boss's son-in-law admits that he only raised the pH to 5.65. However, the son-in-law maintains that the small difference in pH (5.65 vs. 7) is too small to be responsible for the factor of 10 increase in the zinc's corrosion rate (i.e., the zinc lasted less than 1 year, instead of the 10 years you had predicted). The son-in-law claims that your incompetence is responsible for the premature failure of the tank.

    You need to refute the accusation of incompetence made by your boss and his son-in-law against you. There isn't time to measure the corrosion rate of zinc in spent solution of pH 5.65. Using only the data that you already have (i.e., the polarization curves and the measured values of pH), prepare a convincing case that will persuade the plant manager that it was the son-in-law's negligence that is responsible for the early failure of the storage tank.

Info: pH = 7

$\Delta\phi_{corr} = -0.5V$

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

$m_{ox} = 12.5$

$m_{red} = -5.5$

Reduction Rxn:

$H^+ + e^- \rightarrow \frac{1}{2} H_2$

$$\Delta\phi_e(H) = \Delta\phi_e^\circ - \frac{RT}{F} \ln \frac{P_{H_2}^{1/2}}{[H^+]}$$

$$= 0 + 0.0592 \log [H^+]$$

$$= 0.0592 \log [1\times10^{-7}]$$

$$= -0.4144V$$

+~~6~~5

Original Reduction (7):

+6

$\log i = m\Delta\phi + b$

$\log(5\times10^{-7}) = -5.5(-0.5) + b$

$b = -9.05$

$\log i_0 = -5.5(-0.4144) + b$

$i_0 = 1.695\times10^{-7} A/cm^2$

$$-\frac{2F(1-\beta)}{2.303RT} = -5.5$$

$$\frac{1-\beta}{0.0592} = 5.5$$

$\beta = 0.6744$ +4

$$i_0 = D \cancel{P_{H_2}^{(1-\beta)/2}}^{1} [H^+]^\beta \Rightarrow D = \frac{i_0}{[1\times10^{-7}]^\beta} = 0.00891$$ +2

New Reduction (pH 5.65)

$\Delta\phi_e = 0.0592 \log [H^+]$

$= 0.0592 \log [10^{-5.65}] = -0.3345 V$ +~~6~~5

$i_{o,new} = D[H^+]^\beta = 0.00891(1\times10^{-5.65})^{0.6794} = 1.379\times10^{-6} A/cm^2$ +3

$\log i_{o,new} = -5.5\, \Delta\phi_{e,new} + b_{new}$

+2 $\Rightarrow b_{new} = -7.7$

$\log i_{new} = -5.5\, \Delta\phi_{new} - 7.7$

@ $\Delta\phi_{corr}$ Oxidation = Reduction

for oxidation:

$\log 5\times10^{-7} = 12.5(-0.5) + b$

$\Rightarrow b_{ox} = -0.051$

+2

$\log i_{ox} = 12.5\,\Delta\phi - 0.051$

$\Rightarrow 12.5\,\Delta\phi_{corr} - 0.051 = -5.5\,\Delta\phi_{corr} - 7.7$

+3

$\Rightarrow \Delta\phi_{corr,new} = -0.429V$

$\log i_{corr,new} = -5.5(-0.429) - 7.7$

+3

$\Rightarrow i_{corr,new} = 4.796\times10^{-6}\ A/cm^2$

If $i_{corr,new}$ 10x's greater than @ pH = 7 $\Longrightarrow$ son-in-law's fault

$$\frac{i_{corr,new}}{i_{corr}} = \frac{4.796\times10^{-6}}{5\times10^{-7}} = 9.59$$

3. (i) Based on the following information, construct the Pourbaix diagram of beryllium (Be) in water. (ii) Include in your diagram the two lines that mark the region in which water is thermodynamically stable. Identify the equilibrium reaction associated with each line. (iii) Indicate the region of the diagram in which beryllium might be corrosion resistant, even though it is thermodynamically unstable.

(i) 15 pts
(ii) 6 pts
(iii) 3 pts

(i)

$Be^{++} + 2e^- \rightarrow \mathbf{Be}$, $\Delta\phi_e^O = -1.847V$ $\Delta\phi_e = -1.847 + \frac{0.0592}{2}(-6) = \boxed{-2.02V}$

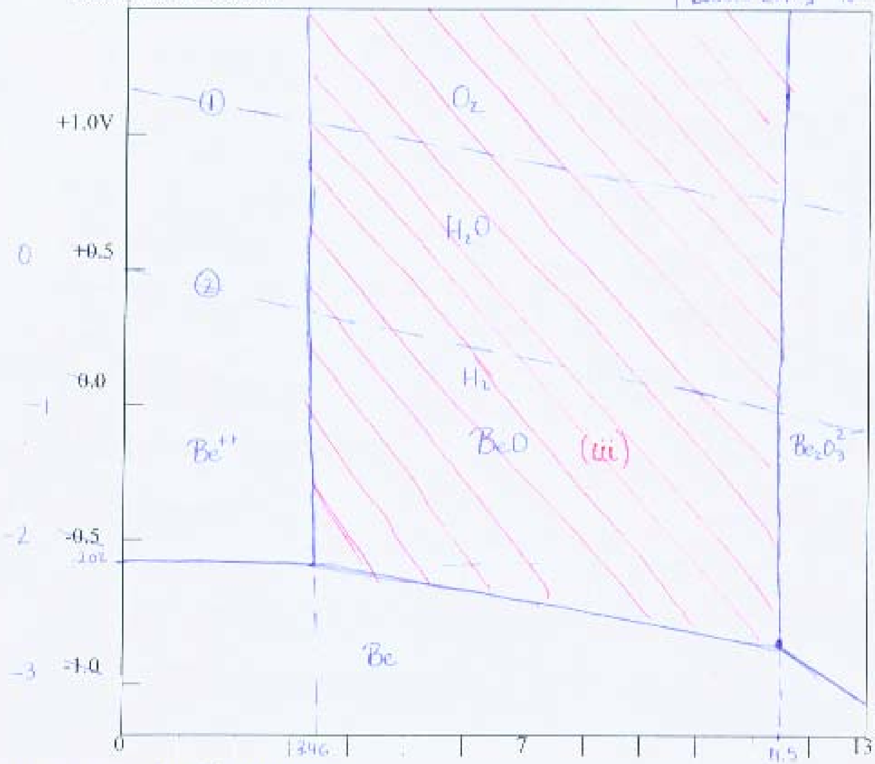
$\mathbf{BeO} + 2H^+ + 2e^- \rightarrow \mathbf{Be} + H_2O$, $\Delta\phi_e^O = -1.820V$ $\Delta\phi_e = -1.820 - \frac{0.0592}{2}\log\frac{1}{[H^+]^2}$ $\boxed{-1.82 - 0.0592\,pH}$

$Be_2O_3^{-2} + 6H^+ + 4e^- \rightarrow 2\mathbf{Be} + 3H_2O$, $\Delta\phi_e^O = -1.391V$ $\Delta\phi_e = -1.391 - \frac{0.0592}{4}\log\frac{1}{[10^{-6}][H^+]^6} = \boxed{-1.48 - 0.0888\,pH}$

$Be^{++} + H_2O \rightarrow \mathbf{BeO} + 2H^+$ $K = 10^{-0.91}$ $10^{-0.91} = \frac{[H^+]^2}{[Be^{++}]}$ $\Rightarrow \boxed{pH = 3.455}$

$2\mathbf{BeO} + OH^- \rightarrow Be_2O_3^{-2} + H^+$ $K = 10^{-15.05}$ $10^{-15.05} = \frac{[BeO_3^{2-}][H^+]}{[BeO]^2[OH^-]} = \frac{10^{-6}[H^+]^2}{10^{-14}}$ $[OH^-][H^+] = 10^{-14}$ $[OH^-] = \frac{10^{-14}}{[H^+]}$ $\boxed{pH = 11.5}$

BOLDFACE => solid



(ii) ① $H_2O + \frac{1}{2}O_2 + 2e^- \rightarrow 2(OH^-)$ $\Delta\phi_e^o = 0.401V$

$\Delta\phi_e = 1.243 - 0.0592\,pH$

② $2H^+ + 2e^- \rightarrow H_2$ $\Delta\phi_e^o = 0V$

$\Delta\phi_e = 0 - 0.0592\,pH$

4. (a) What characteristics of iron's passive film are responsible for its protectiveness against corrosion?

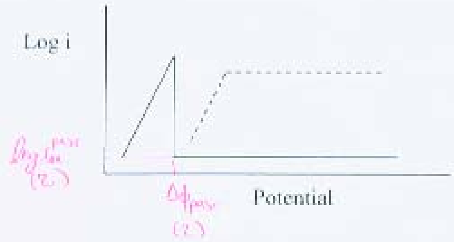
(1) resistance to iron transport (+4)

(2) low solubility of PF in aqueous electrolyte (+1)

(b) In the figure below, the solid curve is a sketch of the kinetics of oxidation of iron in de-oxygenated aqueous borate buffer (pH8.4). Label the passivation potential and iron's oxidation rate in the passive state.

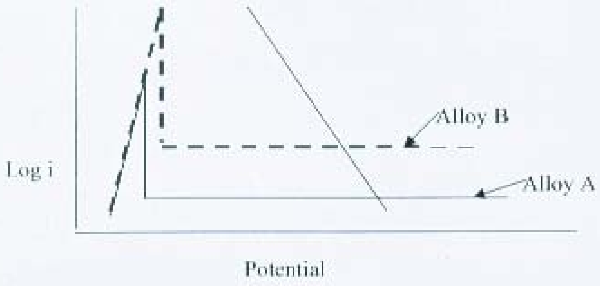
The dashed curve is the total rate of oxidation when iron is immersed in aqueous borate buffer with 2×10^{-4} M of Fe^{++}, as measured by Nagayama and Cohen. What is the product of the extra amount of oxidation of iron in the passive region in {borate buffer + 2×10^{-4} M of Fe^{++}}? Iron Oxide – Fe(III) ~ Fe_2O_3 (5)

Compare the amount of oxidation in the passive state of an iron electrode immersed in borate buffer to the amount of oxidation in the passive state of an iron electrode immersed in {borate buffer + 2×10^{-4}M of Fe^{++}}. In which solution is the amount of oxidation of the iron electrode likely to be greater? Briefly explain your answer.



Amt of oxidation in the electrolyte containing Fe^{+2} will probably be lesser since a thicker passive film will form (3)

(c) The kinetics of oxidation of two alloys in sea water are sketched in the figure, along with the kinetics of reduction of oxygen, which are the same for both alloys. Which alloy, A or B, is likely to be more resistant to crevice corrosion in sea water? List the reasons for your answer.



A more resistant because:

(1) lower passive oxidation rate (2)

(2) lower max oxidation rate (2)

(3) lower value of passivation potential (2)